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SEPTEMBER, 1950

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THE CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING OCTOBER, 1950

LONDON.

Thursday, October 12*th*, 1950, *at* 7.30 *p.m.*

The following papers will be read and discussed :

"The Kinetics of the Oxidation of Organic Compounds by Ceric Sulphate. Part I. The Oxidation of Acetone." By J. Shorter and C. N. Hinshelwood.

"The Kinetics of the Oxidation of Organic Compounds by Ceric Sulphate. Part II. The Reactivities of the Aliphatic Ketones and Acetaldehyde." By J. Shorter.

"Some Oxidation-reduction Reactions of Hydroxylamine." By P. Davis, M. G. Evans, and W. C. E. Higginson.

"Reactions of the Cobaltic Ion. Parts I, II, and III." By C. E. H. Bawn and A. G. White.

Abstracts of the papers for discussion may be obtained from the General Secretary after October 5th.

ABERDEEN.

Friday, October 20*th*, 1950, *at* 7.30 *p.m.*

Lecture, **Recent Work on the Transuranic Elements,** by Dr. R. Hurst, G.M., M.Sc.

Joint meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, Marischal College, Aberdeen.

BIRMINGHAM.

Friday, October 20*th*, 1950, *at* 4.30 *p.m.*

Lecture, **Chemistry and the Scattering of Light,** by Dr. E. J. Bowen, M.A., F.R.S.

Joint meeting with the University Chemical Society to be held in the Chemistry Lecture Theatre, The University, Edgbaston, Birmingham, 15.

EDINBURGH.

Thursday, October 26*th*, 1950, *at* 7.30 *p.m.*

Lecture, **The Scientific Examination of Pictures,** by Dr. A. E. Werner, M.A., A.R.I.C.

Joint meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at the North British Station Hotel, Edinburgh.

EXETER.

Friday, October 13*th*, 1950, *at* 5 *p.m.*

Lecture, **Research in the Paint Industry,** by Dr. J. W. Dorling, A.R.I.C.

Joint meeting with University College Chemical Club, to be held in the Washington Singer Laboratories, Prince of Wales Road, Exeter.

Friday, October 20th, 1950, at 5 p.m.

Lecture, **The Basic Principles of Chemical Engineering,** by Mr. M. B. Donald, M.Sc., A.R.C.S., F.R.I.C.

Joint meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at the Technical College, Plymouth.

GLASGOW.

Wednesday, October 25th, 1950, at 3.30 p.m.

Lecture, **Recent Developments in Macrocyclic Pigments,** by Professor R. P. Linstead, C.B.E., D.Sc., M.A., F.R.S.

Joint meeting with the Alchemists' Club and the Andersonian Chemical Society, to be held at the Royal Technical College, Glasgow.

IRISH REPUBLIC.

Wednesday, October 25th, 1950, at 7.45 p.m.

Lecture, **Editing for The Chemical Society,** by Dr. R. S. Cahn, M.A., F.R.I.C.

To be given in the Chemical Laboratory, Trinity College, Dublin.

MANCHESTER.

Thursday, October 19th, 1950, at 6.30 p.m.

Official Meeting. Lecture, **The Chemistry of the Tropolones,** by Professor R. D. Haworth, D.Sc., F.R.S.

Joint meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Lecture Theatre, The University, Manchester.

NORTH WALES.

Friday, October 13th, 1950, at 5.45 p.m.

Lecture, **Studies in the Synthesis of Flavones,** by Professor T. S. Wheeler, D.Sc., F.R.I.C.

Joint meeting with University College of North Wales Chemical Society to be held in the Department of Chemistry, University College of North Wales, Bangor.

ST. ANDREWS AND DUNDEE.

Friday, October 20th, 1950, at 5 p.m.

Lecture, **Historical Science as an Instrument of Culture,** by Professor J. Read, D.Sc., F.R.S.

Joint meeting with St. Andrews University Chemical Society, to be held in the Chemistry Department, United College, St. Andrews.

SHEFFIELD.

The lecture by Professor C. E. H. Bawn arranged for October 26th, 1950, and entitled **Catalysed Oxidations** has been postponed until February 1st, 1951.

SOUTHAMPTON.

Monday, October 9th, 1950, at 7 p.m.

Lecture, **The New Elements,** by Professor H. J. Emeléus, D.Sc., F.R.S.

Joint meeting with the Mid-Southern Counties Section of the Royal Institute of Chemistry and the Portsmouth and District Chemical Society, to be held at Municipal College, Portsmouth.

SOUTH WALES.

Friday, October **13***th*, **1950**, *at* **5.30** *p.m.*

Lecture, **Some Aspects of the Chemistry of Sulphur Compounds occurring in Nature,** by Professor F. Challenger, D.Sc., F.R.I.C.

Joint meeting with the Royal Institute of Chemistry and University College of Swansea Chemical Society, to be held at University College, Swansea.

PROCEEDINGS
OF THE
CHEMICAL SOCIETY

OFFICIAL ANNOUNCEMENTS

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in November next. All persons who have received grants, and whose accounts have not been declared closed by the Council, are informed that reports must be received by the Society not later than November 1st, 1950.

Applications for grants, to be made on forms obtainable from the General Secretary, must be received on or before November 1st, 1950. Applications from Fellows will receive prior consideration.

Attention is drawn to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is principally devoted to the encouragement of research in inorganic and metallurgical chemistry, and that the income from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

CONFERENCE ON THE BIOLOGICAL HAZARDS OF ATOMIC ENERGY.

A conference, arranged jointly by the Institute of Biology and the Atomic Scientists' Association, with the support of the British Association, on the subject of atomic energy and its biological hazards, will be held at the Royal Institution, Albemarle Street, London, W.1, on October 20th and 21st, 1950. Fellows who are interested are invited.

LIST OF APPLICATIONS FOR FELLOWSHIP

(*Fellows wishing to lodge objection to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of publication of the "* Journal *" for September, 1950. Such objections will be treated as confidential. The forms of application are available in the Library.*)

***Freedman, Patricia,** B.A. (Oxon). British. 29, Abercorn Place, N.W.8. Technical Assistant at British Celanese. *Signed by:* A. M. Spratt, B. F. M. London, J. C. Everett.

***Johnson, Philip Cowey,** B.Sc. and Ph.D. (L'pool.). British. 109, Bramhall Lane South, Bramhall. Research Chemist. *Signed by:* W. B. Whalley, J. S. E. Holker, D. E. Hathway.

Moseley, Philip John, A.R.I.C. British. 264, Pasture Road, Stapleford, Nottingham. Research Chemist. *Signed by:* N. D. Ridsdale, T. A. Heppenstall, J. R. Jarratt.

***Reeve, Keith Desmond,** B.Sc. (Tasmania), A.A.C.I. British. 44, Bayswater Road, Moonah, via Hobart, Tasmania. Demonstrator in Chemistry at University of Tasmania. *Signed by:* G. C. Israel, J. B. Polya, H. E. Hill.

***Schwarz, Johann Claus Peter,** B.A. and B.Sc. (T.C.D.), A.R.I.C. Irish. Department of Chemistry, Trinity College, Dublin. Research Student. *Signed by:* D. H. Hayes, J. A. Alexander, E. R. Stuart.

Warburton, William Kingston, B.Sc. and LL.B. (Sydney). British. McMaster Laboratories, C.S.I.R.O., University Grounds, Sydney, N.S.W. Research Worker. *Signed by:* T. Iredale, S. J. Angyal, A. T. Norman.

UNDER SPECIAL PROVISIONS APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Dutta, Dilip Kumar, M.Sc. (Calcutta), Ph.D. (Sheffield), A.R.I.C., A.M.Inst.F. Indian. Crewe Hall, Clarkehouse Road, Sheffield, 10. Research Scholar. *Signed by:* A. S. C. Lawrence.

***Dokry, Alan Mors,** S.M. (Chicago). American. 1332, West Estes Avenue, Chicago 26, Illinois. Research Assistant, University of Chicago. *Signed by:* R. M. Acheson, Allan P. Gray.

Jacobson, Herbert, S.M. (Chicago). American. 4441, S. Greenwood Avenue, Chicago 15, Illinois. Student. *Signed by:* Allan P. Gray.

Meehan, Francis Thomas, B.Sc. and Ph.D. (L'pool.). British. c/o Imperial Chemical Industries of Australia and New Zealand Ltd., 300, Collins Street, Melbourne, Victoria. Chairman and Managing Director. *Signed by:* David Rivett.

***Roginsky, Adelle L.** B.Sc. (Alberta), M.S. (Chicago). Canadian. International House, 1414-E.59 Street, Chicago 37, Illinois. Student. *Signed by:* R. M. Acheson, Allan P. Gray.

Vaughn, jun., Howard Alton, B.Sc. (Calif.). American. 29, West 601 Street, Orangeburg, New York. Student, Columbia University. *Signed by:* David Y. Curtin.

Zavist, Algerd F., B.S. (Central Y.M.C.A. College), M.S. and Ph.D. (Chicago). American. 4201 W. 48th Street, Chicago 32, Illinois. Research Chemist. *Signed by:* Allan P. Gray, R. M. Acheson.

PAPERS RECEIVED.

(List of papers received between August 1st and August 21st, 1950.)

"The detection of glycosides and non-reducing carbohydrate derivatives in paper partition chromatography." By J. G. Buchanan, C. A. Dekker, and A. G. Long.

"Substituted benzidines and related compounds as reagents in analytical chemistry. Part IV. Naphthidine as indicator in the determination of zinc with ferrocyanide." By R. Belcher and A. J. Nutten.

"Substituted benzidines and related compounds as reagents in analytical chemistry. Part V. New indicators for the microvolumetric determination of gold." By R. Belcher and A. J. Nutten.

"Preparation of benzylidene diacetate." By W. Davey and J. R. Gwilt.

"Experiments with optically active diphenyls." By F. Bell and G. A. Dinsmore.

"The rotatory dispersion and circular dichroism of (−)-2-chloro-2-nitrosocamphane and the pyridine salt of (+)-2-chloro-2-nitrosocamphane-10-sulphonic acid." By Stotherd Mitchell, J. S. Watson, and (in part) W. Dunlop.

"The polarities of molecules containing iodine with a valency higher than one." By (Mrs.) C. G. Le Fèvre and R. J. W. Le Fèvre.

"Experiments on the synthesis of the pyrethrins. Part V. Synthesis of side-chain isomers and analogues of cinerone, cinerolone, and cinerin-I." By L. Crombie, A. J. B. Edgar, S. H. Harper, (Miss) W. M. Lowe, and D. Thompson.

"The mechanism of inhibition of the corrosion of iron by sodium hydroxide solution." By J. E. O. Mayne, J. W. Menter, and M. J. Pryor.

"The equilibrium between copper and cupric and cuprous ions, and the behaviour of the copper electrode in dilute copper sulphate solutions." By S. E. S. ElWakkad.

"Quaternary ammonium salts. The formation and decomposition of ethyldimethylphenylammonium salts. The synthesis of *N*-ethyl-*N*-methylanilines." By Hussein A. Fahim and Mohamoun Galaby.

"The oxidation of aldoses by hypoiodous acid. Part III. Comparison of the rates of oxidation of α- and β-D-glucose." By K. D. Reeve.

"Perhydroindanes. Part I. Some products from β-(1-hydroxy*cyclo*hexyl)propiolic acid." By David S. Mathieson.

"Further studies on the stereochemistry of aromatic ethers." By K. B. Everard and L. E. Sutton.

"The conductivities of some complex cobalt chlorides and sulphates." By I. L. Jenkins and C. B. Monk.

" Fission of the alkyl-oxygen bond in carbinols and of the alkyl–sulphur bond in sulphides and sulphones." By M. P. Balfe, J. Kenyon, and C. E. Searle.

" 4-Hydroxy-2′ : 3′-dimethoxybenz*cyclo*heptatrien-3-one and related topics." By J. A. Barltrop, A. J. Johnson, and G. D. Meakins.

" The synthesis of simple peptides from anhydro-*N*-carboxyamino-acids." By J. Leggett Bailey.

" Structure of an antigenic polysaccharide isolated from tuberculin." By P. W. Kent.

" Carbohydrate primers in the synthesis of starch." By J. M. Bailey, W. J. Whelan, and S. Peat.

" The enzymic synthesis and degradation of starch. Part X. The phosphorylase and Q-enzyme of broad bean. The Q-enzyme of wrinkled pea." By P. N. Hobson, W. J. Whelan, and S. Peat.

" The enzymic synthesis and degradation of starch. Part XI. Isophosphorylase." By J. M. Bailey and W. J. Whelan.

" Dimorphism of esters of *scyllo*inosose." By S. J. Angyal and N. K. Matheson.

" Researches on acetylenic compounds. Part XXVII. The preparation and properties of the toluene-*p*-sulphonates of acetylenic alcohols." By G. Eglington and M. C. Whiting.

" Photochlorination. Part I. The photochlorination of toluene vapour." By Mowbray Ritchie and W. I. H. Winning.

" Photochlorination. Part II. The photochlorination of methane." By Mowbray Ritchie and W. I. H. Winning.

" Reactions of the perfluoroalkyl radicals." (Miss) J. Banus, H. J. Emeléus, and R. N. Haszeldine.

" Contributions to the chemistry of phenanthridine. Part II. The preparation of 2 : 7-diamino-9-3′-pyridylphenanthridine 1′ : 10-dimethiodide." By V. Petrow and W. R. Wragg.

" Alternative method for the hydrolysis of thioamides in the Willgerodt–Kindler reaction." By M. A. Thorold Rogers.

" Hydrated calcium silicates. Part I. Compound formation at ordinary temperatures." By H. F. W. Taylor.

" The electric dipole moments of some tetrazolines and related compounds." By P. G. Edgerley and L. E. Sutton.

" Tertiary perfluoro-amines." By R. N. Haszeldine.

" The determination of thionaphthen in naphthalene by infra-red absorption spectroscopy." By W. D. Armstrong, A. B. Densham, and G. Gough.

" The colour of organic compounds. Part I. A general colour rule." By Edward B. Knott.

" The colour or organic compounds. Part II. The replacement of chromophoric methin groups by nitrogen atoms." By Edward B. Knott.

" The colour of organic compounds. Part III. Colour phenomena of bis-2-(3 : 5-diphenylpyrrole)methins." By Edward B. Knott and Roy A. Jeffreys.

" Monolayer properties of elaidyl alcohol." By J. Glazer and E. D. Goddard.

" Reactions of ethylene oxides. Part V. The interaction of alkali cyanides and epichlorohydrin." By C. C. J. Culvenor, W. Davies, and F. G. Haley.

" Hantzsch's isomeric diazosulphonates." By H. C. Freeman and R. J. W. Le Fèvre.

" Synthesis of 8-substituted pteridine derivatives." By H. S. Forrest, R. Hull, H. J. Rodda, and A. R. Todd.

" The effects of intramolecular configuration on the rate of unimolecular solvolysis of aralkyl chlorides." By G. Baddeley and J. Chadwick.

" The optical properties of 2-amino-*n*-octane, 2-dimethylamino-*n*-octane, and trimethyl-2-*n*-octylammonium iodide." By F. G. Mann and (Mrs.) J. Reid.

" Molecular polarisation and molecular interaction. Part IV. The molecular polarisation of diphenylamine in solution in benzene, dioxan, and mixtures of benzene with nitrobenzene, triethylamine, and pyridine." By J. W. Smith.

"Pteridines. Part I. An unambiguous synthesis of 7 : 8-dihydro-6-hydroxypteridines." By W. R. Boon, W. G. M. Jones, and G. R. Ramage.
"The condensation of 2-dimethylaminomethylcyclohexan-1-one with acetylenic compounds." By R. A. Raphael and Franz Sondheimer.
"The chemistry of extractives from hardwoods. Part III. Baikiain, an amino-acid present in *Baikiaea plurijuga*." By F. E. King, T. J. King, and A. J. Warwick.
"Entropies of vaporization, and internal order in liquids." By L. A. K. Staveley and W. I. Tupman.

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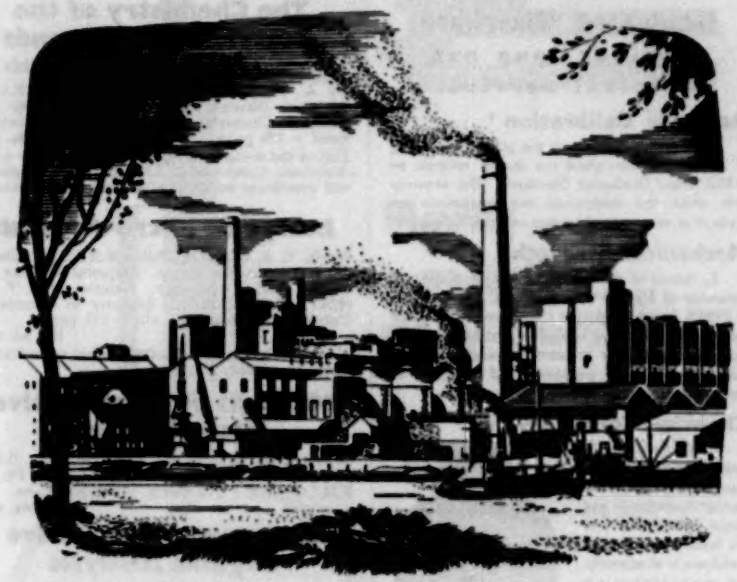

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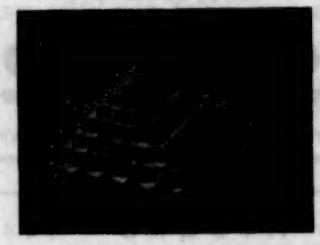

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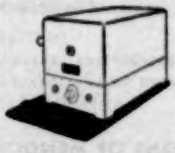

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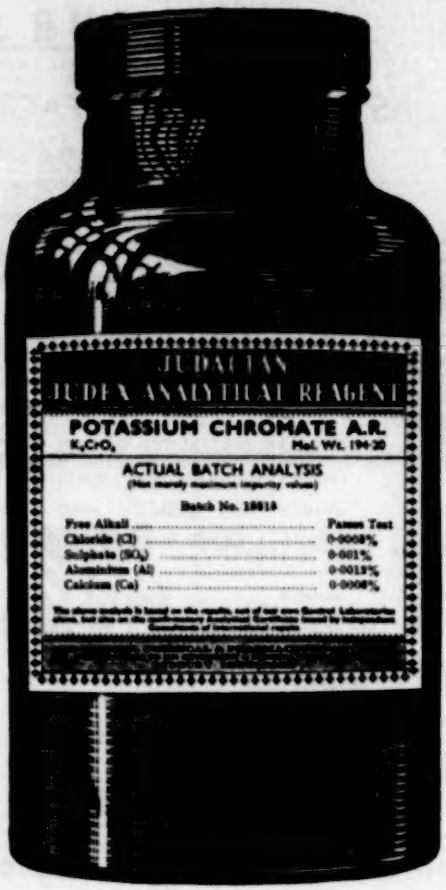

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INFORMATION FOR CANDIDATES FOR FELLOWSHIP

The Chemical Society was founded in 1841 and received a Royal Charter in 1848.

The main function of the Society is to foster original research in chemistry and to facilitate the discussion and dissemination of new knowledge in all branches of the science.

Fellowship of the Society is open to men and women of all nationalities who are interested in chemistry and wish to keep in touch with its advances. Fellows are elected by the Council.

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2. To consult and borrow the books in the Library.
3. To attend meetings of the Society both in London and outside London, and to introduce two guests thereto.
4. To apply for research grants.
5. To submit original papers for publication in the *Journal*.

Fellows under the age of 25, who so wish, may pay an annual subscription of £1 15s. and enjoy all the privileges accorded to those paying the full subscription except that the choice of publications is limited.

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(*a*) *The Journal of the Chemical Society*, which is published monthly, contains the results of investigations which cover the whole field of pure chemistry.

(*b*) *British Abstracts*.—The Society collaborates with the Society of Chemical Industry, the Physiological Society, the Biochemical Society, and other organisations in contributing to the maintenance of the Bureau of Abstracts, which issues every month abstracts of papers dealing with all branches of pure and applied chemistry, physiology, and anatomy published in all parts of the world.

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(*c*) *Annual Reports on the Progress of Chemistry*.—These reports, written by experts, summarise the important new advances in pure chemistry and related subjects.

(*d*) *Quarterly Reviews* are composed of articles on selected topics from the whole field of chemistry.

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MEETINGS

(*a*) *In London*.—Scientific Meetings of the Society are held usually on the first and third Thursdays of each month from October to June at Burlington House, at which papers dealing with original work are read and discussed, organised discussions on subjects of current interest are arranged, and lectures by eminent British and foreign chemists are delivered.

(*b*) *Outside London*.—Scientific Meetings and lectures arranged by the Society's Local Representatives are also held outside London, and form an important part of the activities of the Society.

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A Research Fund is available for the assistance of chemical research, and sums amounting annually to about £700 are granted for this purpose. Application for grants must be made on the appropriate form, which may be obtained from the General Secretary.

Forms of Application for Fellowship can be obtained from THE GENERAL SECRETARY, THE CHEMICAL SOCIETY, BURLINGTON HOUSE, PICCADILLY, LONDON, W.1.

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SUBMISSION OF PAPERS. 1. All Scientific Communications for the *Journal* should be addressed to "The Honorary Secretaries, The Chemical Society, Burlington House, W.1." Papers to be read before a meeting of the Society are selected by the Honorary Secretaries.

2. A paper is not normally considered for publication in the *Journal* unless at least one of the authors is a Fellow of the Society, but in exceptional circumstances the Council is prepared to consider papers submitted by non-Fellows.

3. Communications which have appeared or have been accepted for publication with essentially the same scientific content in another Journal or freely available printed work shall not be published in the *Journal* of the Society unless this course is approved by the Council.

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RESPONSIBILITY. 8. Authors are solely responsible for the factual accuracy of their papers. They are particularly requested to verify references and to indicate positions of cross-references.

SUMMARY. 9. Every paper must be prefaced by a short summary (50—250 words) setting forth briefly and in simple language the objects of the investigation and the results obtained. The summary should give any chemist a clear idea of what the investigation has achieved and should be independent of the main text. "Notes" do not require a summary.

STYLE. 10. Authors are requested to see that their papers conform, as nearly as possible, to the normal style, conventions, and conciseness of the *Journal*.

NOMENCLATURE. 11. Authors are expected to be familiar with the normal rules of nomenclature, but are invited to communicate with the Editor if in doubt or in special cases. Some of the principles followed in the *Journal* are reviewed in "Modern Chemical Nomenclature," by Dr. Clarence Smith (*J.*, 1936, 1067); reprints of this paper may be obtained by Fellows, price 2*d.* post free, from the General Secretary. Much valuable discussion will be found in "British Chemical Nomenclature," by Dr. A. D. Mitchell [Edward Arnold & Co., 1948]. Authors should choose their symbols from the "Report of a Joint Committee of the Chemical Society, Faraday Society, and the Physical Society on Symbols for Thermodynamical and Physico-Chemical Quantities and Conventions Relating to their Use," copies of which may be obtained by Fellows, price 4*d.* post free, from the General Secretary.

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ILLUSTRATIONS. 13. Illustrations accompanying the papers must be carefully drawn, preferably *twice* the size of the finished block (max. width 5 inches), *in Indian ink, on good white cartridge paper* (graph paper with faint blue lines is acceptable). Any illustration which seriously exceeds four times the size of the finished block will be returned to the author for re-drawing to a smaller scale. Lettering on the drawings, whether on the margin or in the body of the drawing, must not be in ink but must be inserted *clearly but lightly in pencil*. *Margins* of at least two inches must be left. Authors may, if they wish, submit in the first place clearly drawn pencil sketches instead of the completed diagrams, which, however, must be supplied before publication. Further information can be obtained from the Editor.

PROOFS. 14. Authors will be expected to pay the cost of any considerable changes made by them in proof, apart from the correction of printers' errors. See also paragraph 7.

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1945 and on which he served until 1948 when he declined re-nomination. He was elected Chairman of Convocation in 1948.

The Principal of the University has kindly supplied the following appreciation. "Throughout the last 23 years of his life he was a well-known figure in University affairs and rendered valued services to the University as an 'elder statesman' during the last five years of his life. He took a leading part in the discussions of the post-war plans of the University and was Chairman of two important Councils, the Finance and General Purposes Committee and the External Council. In his capacity as Chairman of the External Council he had much to do with the development of more intimate relations between the University and the four university colleges which still take the External degree of the University of London."

Other Services to Education.—He became a member of the Surrey Education Committee, as a representative of London University, when it was reconstituted after the Education Act of 1944, and he served on the Secondary Education and the Further Education Committee and became especially interested in the work of the latter where his advice and knowledge were highly esteemed.

He gave the Committee great help in drawing up and administering their scheme for Award of Major Scholarships and Exhibitions to students taking university courses, and also in planning the expansion of higher technological education in the County.

A development which took place during his period of service was the decision of the County Council to make an annual grant of nearly £30,000 to the University of London.

The Chief Education Officer writes: "It is very unusual for a member who is not a member of the County Council to be selected to Office on the Surrey Education Committee but Sir Robert Pickard was so highly esteemed by his colleagues that they selected him Vice-Chairman of the Further Education Committee."

He served as Honorary Secretary of the teachers' panel of the "Burnham Committee" dealing with salaries for teachers in technical colleges and art schools, 1922—1925, and from 1920 to 1923 was a member of the Consultative Committee of the Board of Education. From 1930 to 1940 he was a Member of Council of Manchester High School for Girls and from 1940 to 1948 Chairman of the Governing Body of Roedean School.

He served as a Member of Council of the Leatherseller's Technical College from 1924 to 1948.

He was also at different times a member of the Courts of the Universities of Birmingham and Manchester.

Royal Institute of Chemistry.—Pickard became a Fellow of the Institute of Chemistry in 1902 and in later years developed a keen interest in its affairs, particularly those concerned with the education and training of chemists. He was a member of its Council during the periods 1923—1926, 1944—1946; Vice-President 1927—1930, 1939—1943; President 1936—1939 and Censor 1936—1944.

During his Presidency he delivered the eighth Gluckstein Memorial Lecture (in 1936) with the title "An Experiment in Co-operative Research in the Cotton and Other Textile Industries" in which he summarised his views and experience as the Director of a large Research Association.

Chemical Society and Chemical Council.—Pickard joined the Chemical Society in 1897 and served on the Council, 1916—1920, 1926—1928, and as Vice-President, 1931—1934, 1937—1940: he was for many years a very regular attendant at the Society's meetings. The Historical Review of the Chemical Society 1841—1941 states (p. 154): "In the Society he has for years been a watchful and outspoken critic of its methods and organisation and his criticism has been constructive. He was one of those who proposed the formation of a Reconstruction Committee in 1932 and was its most active member. The various recommendations of this important committee were put into effect and resulted in an extension and an invigoration of the Society's activities. His foresight and experience have been of great value to the Finance and General Purposes Committee, on which he served for several years, and to Council. Directly, in such activities as these, and indirectly as Chairman of the Chemical Council (1931—1938), he had a great influence on the development of the Society in the last decade."

Industrial Research.—Pickard's experience in Lancashire had led him to a deep-rooted belief, to which he frequently gave expression, that the application of the results of fundamental research to industrial processes would result in valuable technological developments, and he told the writer of this Notice that pressure was exerted on him about 1920 to take an active interest in the new Research Association movement. It is certain that the pressure only needed to be gentle to start him off on this course, since his inclinations had been tending in this direction for some time, and his desire for an administrative post of the type afforded by the supervision of a research association had been steadily growing. His recognition that the

undertaking of long-range investigations would constitute an essential part of the work of research associations led to his becoming a champion of co-operative research associations in general.

The growth of the Research Association movement is the most marked development in the organisation of industrial research in this country since the first world war, and there can be no doubt that the movement's present vitality and vigour owe much to Pickard's long participation.

British Leather Manufacturers' Research Association.—In 1920 Pickard, on the strong recommendation of a representative committee, became the first Director of the newly-formed British Leather Manufacturers' Research Association and was quick to seize the opportunities afforded by such an appointment. These activities he combined with his duties as Principal of Battersea Polytechnic which he had assumed earlier in the same year, and his resolution and capacity for work enabled him to do justice to these combined responsibilities.

He now proceeded to transform his beliefs into practice and show how science should be applied to industry. He soon recognised that the histology of hides and skins and the physico-chemical examination of tanning solutions and of proteins were of fundamental significance in attempting to deal with the difficulties which, despite centuries of empiricism, still confront the leather manufacturer, and accordingly he gathered together a highly competent staff of research workers which included the late Dr. D. Jordan-Lloyd amongst its first members.

He soon became convinced that if an industry was to receive substantial benefit from its research association the work of the staff must be made known to and applied by members of the industry, and so visits to works and surveys of processes were arranged and organised. Although he was Director for only 7 years he maintained his connexion with the British Leather Manufacturers' Research Association, in the first place as consultant and later as honorary consultant, until the time of his death.

He was a loyal and devoted servant of the leather industry, pre-eminently as a planner and an organiser, and in these capacities he rendered notable service which has been freely recognised by the industry as a whole: he did not attempt to make any profound contribution to the scientific studies of the research association.

In recognition of his services to education and to the application of scientific research to industrial processes he was elected an Honorary Liveryman of the Leathersellers' Company in 1938.

British Cotton Industry Research Association.—Of Pickard's numerous activities the one with which his name is most closely associated is that of his Directorship of the British Cotton Industry Research Association—a post to which he was appointed at the age of 53 whilst still alert and vigorous, with a varied experience behind him which included an "apprenticeship" of 7 years as Director of the British Leather Manufacturers' Research Association.

When the Directorship of the Cotton Research Association fell vacant in 1927 through the death of Dr. A. W. Crossley the post was advertised but Pickard would not apply. It is no secret that he had felt some disappointment at not being called to fill the position when the Research Association was formed in 1919. Fortunately there were those in Lancashire who realised that Pickard was the man for the post and a deputation came to London and induced him to return to Lancashire. Thus he entered on what proved to be the most fruitful period of his career.

He found that a vast amount of first-class scientific knowledge had been accumulated, but that after six years the industry was getting impatient and looking for more practical results. He saw that the time was opportune for an intensive application of the knowledge already gained and for the introduction of special means to link the scientists more closely and effectively with the practical men from the mills, and in 1928 a liaison officer was appointed and a liaison department formed. At the same time investigations of both a fundamental and a technological character were actively pursued and on a steadily increasing scale, so much so that several extensions of accommodation had to be provided during the ensuing 15 years—including a three-story block of laboratories and a large work room to house weaving machinery, which were formally opened in 1936 by the late Lord Derby.

Pickard tackled with understanding the special difficulties facing the Director of a large research association in an industry divided into several distinct sections, *e.g.*, spinning, weaving, bleaching, and finishing. He came to realise that one important function of such a research association is to envisage the industry as a whole rather than as a collection of component groups of firms with sectional interests and requirements.

The success of his policy taken in combination with the life and vigour he infused into the

Shirley Institute community may be gauged from the fact that when he retired after 17 strenuous years the Research Association was recognised on all sides as an essential part of the textile industry and its name was known throughout the world.

By the time he had retired in 1943 the Shirley Institute with a staff of more than 350, including 80 graduates, had become a splendid organisation in the building up of which he had exerted all his powers of initiative, drive, and administrative ability, and in which he took great pride.

Pickard regarded his stay at the Shirley Institute as the most congenial and productive period of his career—it certainly provided an opportunity where his unusual combination of qualities could be exercised to the full.

In all councils and committees of which he was a member, Pickard expressed his views and opinions with clarity and force—on occasions not unmixed with a modicum of truculence—and was always listened to with attention even by those who disagreed with him. His information on matters of fact was always valuable and there were many occasions on which he was able to draw attention to the terms of Government orders or other official decisions which had escaped the notice of his colleagues but which were highly relevant to the subject under discussion.

He was fond of attending committee meetings and, apart from very occasional lapses into impatience, he was an admirable committee man : the agenda had been carefully studied and pondered on and it was seldom that he failed to contribute at least one useful or constructive suggestion.

During this period of office as Vice-Chancellor of the University of London the Board of Studies in Chemistry gave a dinner in Pickard's honour, at which the late Professor J. C. Philip made the well-received jest " What we all admire about Pickard is his downrightness—not that that excludes uprightness ! " Both downrightness and uprightness were indeed the salient qualities of the man.

To the end he was a personality and a man of affairs, frank and fearless in manner. His highly developed critical faculty was in frequent evidence, but in turn he accepted criticism without resentment and usually respected the more highly those who could return some of his critical sallies.

To some his outward bearing was rather aloof or even harsh, but to know him intimately was to recognise a very human man with a high sense of moral values, whose word was his bond.

In 1901 he married Ethel Marian, daughter of Henry Wood of Edgbaston and Dudley and had one son and one daughter. He was created Knight Bachelor in the Coronation Honours of 1937. His family life was a happy one until a few years ago when he suffered two severe blows in the death of his wife and shortly afterwards of his only daughter. He leaves an only son, at whose home in Surrey he died in his sleep.

I am indebted to the Registrar of the Royal Institute of Chemistry, to Dr. F. C. Toy, C.B.E., of the Shirley Institute, and to Dr. H. Phillips, Director of The British Leather Manufacturers' Research Association, for help in the compilation of this notice.

J. Kenyon.

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464. *The Reactions of Certain Epoxides in Aqueous Solutions.*

By W. C. J. Ross.

The reactions of several mono- and di-epoxides have been studied, a new method being used for the determination of epoxides in dilute aqueous solution. Evidence has been obtained for the view that the reactions proceed by the combined action of an acid and a base, and the effect of substituents upon the rate of reaction can be interpreted on this basis. The results are discussed in relation to the biological action of the various epoxides.

A number of attempts have been made to relate the biological effects of the mustard-gas types of compound with their chemical reactivity. The suggestions that mustard gas acts by the liberation of intracellular acid or that it is converted in the tissues into a reactive sulphone were once current but they have been rejected by Peters and Walker (*Biochem. J.*, 1923, **17**, 260). A more recent hypothesis was that of Barron, Bartlett, and Miller (*J. Expt. Med.*, 1948, **87**, 489) who believed that " nitrogen mustard-gas " derivatives could act as structural inhibitors of enzymes because of the similarity between choline and acetylcholine and the ethyleneimonium

ions derived from these "mustards." It is doubtful whether the latter hypothesis covers the case of more complex aliphatic "nitrogen mustards" or of the aromatic "nitrogen mustards" which do not appear to yield ethyleneimonium ions (Ross, *J.*, 1949, 1972). It would now seem that the characteristic feature of all the mustard-gas types of compound which exhibit "radiomimetic" properties (Boyland, *Biochem. Symposia*, 1948, No. 2, p. 67) is their ability to act as difunctional electrophilic reagents under mild conditions in aqueous solution (Davis, Everett, and Ross, *J.*, 1950, 1331).

Epoxides are known to act as electrophilic reagents under these same conditions and it has been demonstrated that they react readily with proteins at physiological pH (Fraenkel-Conrat, *J. Biol. Chem.*, 1944, **154**, 227). This led to the testing of various diepoxides and the establishment of their radiomimetic properties (Loveless and Revell, *Nature*, 1949, **164**, 938; Davis, Everett, and Ross, *loc. cit.*; Bird, in the press).

In the case of the aromatic "nitrogen mustards" the efficiency of a compound as a tumour-growth inhibitor runs parallel with its relative reactivity towards nucleophilic centres, a property conveniently assessed by measuring the rate of hydrolysis in aqueous acetone (Haddow, Kon, and Ross, *Nature*, 1948, **162**, 824). Since this hydrolysis proceeds by an S_N1 mechanism, one is, in effect, measuring the rate of production of carbonium ions from the arylhalogenoalkylamine. One object of the present work was to discover whether a similar correlation between the biological activity of various diepoxides and their reactivity towards nucleophilic centres could be established. Brønsted, Kilpatrick, and Kilpatrick (*J. Amer. Chem. Soc.*, 1929, **51**, 428) have shown that when an epoxide reacts in aqueous solutions containing anions the following reactions take place:

$$(1)\quad H_2O + R\text{-}CH\text{-}CH_2 \xrightarrow{k_1} R\text{-}CH(OH)\text{-}CH_2\text{-}OH + H^+ + OH^-$$

$$(2)\quad H_2O + R\text{-}CH\text{-}CH_2 + H_3O^+ \xrightarrow{k_2} R\text{-}CH(OH)\text{-}CH_2\text{-}OH + H^+ + H_2O$$

$$(3)\quad H_2O + R\text{-}CH\text{-}CH_2 + A^- \xrightarrow{k_3} R\text{-}CH(OH)\text{-}CH_2A + OH^-$$

$$(4)\quad H_3O^+ + R\text{-}CH\text{-}CH_2 + A^- \xrightarrow{k_4} R\text{-}CH(OH)\text{-}CH_2A + H_2O$$

(1) and (3) being the "spontaneous" addition of water and anion respectively and (2) and (4) the corresponding acid-catalysed reactions.

The reaction with anions (3) liberates hydroxyl ions and proceeds at a velocity which is independent of pH over the range 4—8·5, but Brønsted *et al.* (*loc. cit.*) have suggested that the reaction might be reversed at higher pH and have shown that more rapid acid-catalysed reactions occur when the pH falls below 4·2 (see also below). To measure the reactivity of an epoxide towards anions it is therefore necessary to be able to determine the amount of hydroxyl ion liberated and to keep the pH within the prescribed limits; both these conditions may be satisfied by the continous titration of the reaction mixture with a weak acid.

Most organic anions react slowly with epoxides so that in order to be able to make a rapid comparison of the relative reactivities of a range of compounds the strongly nucleophilic thiosulphate ion was used—compare the high reactivity of this ion towards the carbonium ions derived from di-2-chloroethyl sulphide (Ogston, *Trans. Faraday Soc.*, 1948, **44**, 45), the aliphatic "nitrogen mustards" (Golumbic, Fruton, and Bergmann, *J. Org. Chem.*, 1946, **11**, 518), and their aromatic analogues (Ross, *J.*, 1949, 2589).

Since a number of the epoxides examined were sparingly soluble in water it was necessary to measure the comparative reactivities in aqueous acetone. In the method finally adopted the epoxide was added to a boiling 0·2N-solution of sodium thiosulphate in 50% acetone containing phenolphthalein as indicator and the alkalinity which developed was continuously titrated with 0·2N-acetic acid; the rate of addition of acid was proportional to the rate of ester formation. Under these conditions changes in the composition of the solvent caused by the addition of aqueous acid and the effect of added acetate ions were not significant, for the unimolecular rate coefficient calculated from equation (i) below was reasonably constant. With epoxides of the general formula $R\text{-}CH\text{-}CH_2$ (O) the reaction with the thiosulphate ion was quantitative, negligible amounts of glycol being formed so that (viii) (see below) becomes simplified to:

$$k' = \frac{2{\cdot}303}{t} \log_{10} \frac{100}{100 - \%\ \text{ester formed}} \qquad \text{(i)}$$

For more heavily substituted epoxides some glycol was formed under the standard conditions and the ratio x/y was calculated from :

$$\frac{100 - \%\text{ ester formed at } t = \infty}{\%\text{ ester formed at } t = \infty} \quad \ldots\ldots\ldots \quad (ii)$$

and this value was employed to calculate k'(thio), equation (viii) being used. In some cases, particularly of unsymmetrical diepoxides, the value of k' was not constant throughout the whole course of the reaction and in these cases the figures given in Table I are those calculated for 20% and 80% reaction : the results are discussed below.

TABLE I.

Correlation of the chemical reactivity of various epoxides with their biological activity.

Compound.	$100k'$ (thio), min.$^{-1}$.	Toxicity, LD_{50} mg./kg.[a]	Tumour-growth inhibition.[b]
Methiodide of *NN*-di-(2 : 3-epoxypropyl)-*p*-anisidine ...	370	100	—
Epichlorohydrin	130	218	—
Glycidol	115	300	—
1 : 2-3 : 4-Diepoxybutane *	85	25	+
Di-(2 : 3-epoxypropyl) ether *	69	50	+
Ethylene oxide	67		
Bigot's " diallyl dioxide "	60		—
p-Di-(2 : 3-epoxypropoxy)benzene, m. p. 114° †	55	170	+
p-Di-(2 : 3-epoxypropoxy)benzene, m. p. 90° †	55	150	—
m-Di-(2 : 3-epoxypropoxy)benzene †	55	200	—
1 : 2-3 : 4-Diepoxy-2-methylbutane *	53—44	100	+
2 : 4 : 6-Tri(ethyleneimino)-1 : 3 : 5-triazine	44	2	+
1 : 2-5 : 6-Diepoxyhexane	40	97	+
Ethyl di-(2 : 3-epoxypropyl)acetate.....	38	1000	—
Propylene oxide	36	500	—
NN-Di-(2 : 3-epoxypropyl)-*p*-anisidine	26	200	—
Butadiene monoxide	24·6	160	—
1 : 2-5 : 6-Diepoxy-2 : 5-dimethylhexane *	23·4	800	—
p-Divinylbenzene dioxide *	19·8	180	—
1 : 2-3 : 4-Diepoxy-2 : 3-dimethylbutane *	21·2—14·3		—
1-Vinylhex-3-ene dioxide *	13·3—11·3	500	—
*cyclo*Hexene oxide	5·7	500	—
2 : 3-6 : 7-Diepoxy-2 : 6-dimethyloctane (dihydromyrcene dioxide) *.....	5·7—1·4	1000	—
Limonene dioxide *	3·9—2·1	1100	—
1 : 2-3 : 4-Diepoxy-1 : 4-dimethylbutane *	2·3—1·6		—
1 : 2-3 : 4-Diepoxy-1 : 4-diphenylbutane *	0·4	1000	—
Divinyl sulphone	57—39		—
Acraldehyde	3·6—1·8		
Acrylonitrile	0·5		

* The preparation of these compounds will be described in a later communication by Prof. G. A. R. Kon and Mr. J. L. Everett.

† Werner and Farenhorst, *Rec. Trav. chim.*, **1948**, **67**, 438.

[a] Administered in arachis oil to mice by an intraperitoneal injection. [b] Measured against the transplanted Walker rat carcinoma.

Since the reaction of simple epoxides with thiosulphate in 50% acetone is quantitative it provides a convenient method for the determination of such epoxides in aqueous solution. By adding an equal volume of acetone and then sodium thiosulphate to make the solution 0·2M. and titrating the alkalinity formed, the rate of disappearance of epoxide from aqueous solutions under a variety of conditions can be followed. Earlier methods for the quantitative determination of epoxides, such as those of Lubatti (*J. Soc. Chem. Ind.*, 1944, **63**, 133), Nicolet and Poulter (*J. Amer. Chem. Soc.*, 1930, **52**, 1186), and King (*Nature*, 1949, **164**, 706), are not easily adapted to the determination in dilute aqueous solutions.

The rates of reaction of several mono- and di-epoxides in completely aqueous solution have been studied by using this method of determination. Table II shows the rate at which these epoxides react (*a*) with water alone to form glycol and (*b*) with 0·1M-sodium acetate to form ester and glycol at 37°—these conditions approximate more closely to those encountered within cells than those used to determine the order of activity as in Table I, but unfortunately they can only be used for the more water-soluble compounds. There is a considerable difference in the relative amounts of reaction with water and with anion when the reaction proceeds in water alone, as compared with the reaction in 50% acetone—more ester being formed in the latter

case. This is one of the reasons for adding acetone before determining the amount of epoxide in solution by the thiosulphate method.

TABLE II.

Reaction of epoxides with (a) *water and* (b) *water containing* 0·1M-*sodium acetate and* 0·1N-*acetic acid*. (Concn. of oxide, 0·1M. for monoepoxides and 0·05M. for diepoxides. Temp. 37°.)

	(a)		(b)			
Time, hrs.	% epoxide reacting.	k_1, hr.$^{-1}$.	% ester formed.	% epoxide reacting.	k_1, hr.$^{-1}$.	k' (Ac), hr.$^{-1}$.
Glycidol.						
24	15·6	0·0071	7·8	22·8	0·0071	0·0036
48	28·6	0·0070	13·4	39·2	0·0068	0·0035
72	40·0	0·0071	17·8	52·4	0·0068	0·0035
96	49·3	0·0071	22·0	64·0	0·0070	0·0037
Epichlorohydrin.						
24	36·5	0·019	20·6	52·0	0·0185	0·012
48	59·0	0·0185	30·0	76·6	0·0185	0·012
72	72·5	0·018	34·8	88·0	0·018	0·0115
100	84·5	0·0185	38·0	96·0	0·0185	0·013
169	96·5	0·020	39·6	100·0	—	—
1 : 2-3 : 4-*Diepoxybutane.*						
24	15·5	0·0070	11·1	26·3	0·0074	0·0055
48	28·2	0·0069	17·5	45·0	0·0075	0·0052
72	37·4	0·0065	22·1	55·6	0·0068	0·0045
96	43·5	0·0062	25·7	64·0	0·0065	0·0043
168	60·3	0·0055	30·7	78·5	0·0056	0·0037
264	68·6	0·0044	34·2	88·2	0·0050	0·0033
1 : 2-5 : 6-*Diepoxyhexane.*						
6	13·0	0·023	2·4	27·0	0·046	0·0043
24	42·0	0·023	6·05	71·0	0·047	0·0044
32	52·8	0·023	6·75	79·5	0·047	0·0044
48	68·0	0·024	7·75	90·2	0·045	0·0042
72	81·0	0·023	7·85	96·0	—	—
96	89·0	0·023	—	—	—	—
Di-(2 : 3-*epoxypropyl*) *ether.*						
24	15·5	0·0071	6·6	21·8	0·0071	0·0031
48	28·0	0·0069	12·2	40·1	0·0074	0·0032
75	39·6	0·0067	16·8	54·5	0·0072	0·0032
95	47·0	0·0067	19·8	62·5	0·0071	0·0033
119	53·0	0·0065	23·0	72·6	0·0074	0·0034
170	67·8	0·0067	27·0	83·3	0·0071	0·0034
1 : 2-5 : 6-*Diepoxyhexane.**						
24	5·5	0·0024	4·6	13·0	0·0037	0·0021
48	9·5	0·0023	9·2	24·0	0·0038	0·0022
72	—	—	12·8	35·4	0·0038	0·0022
96	19·0	0·0022	16·0	45·5	0·0041	0·0022
144	25·0	0·0020	—	—	—	—
173	—	—	21·1	65·5	0·0041	0·0020
192	30·0	0·0019	—	—	—	—
245	—	—	24·8	77·5	0·0041	0·0020
269	38·4	0·0019	—	—	—	—
342	44·5	0·0017	—	—	—	—

* In these experiments 50% acetone was used as solvent in place of water.

Brønsted *et al.* (*loc. cit.*) studied the reactions of several monoepoxides in aqueous solution, using a method similar to that now adopted, but they were not able to measure the rate of disappearance of epoxide in the same experiments as the rate of ester formation. The coefficient for the rate of reaction of the oxide with water was determined separately by a dilatometric method in the absence of salts and then in the presence of varying concentrations of a salt—sodium perchlorate—which had been shown not to react to form an ester. In this way the variation of the rate coefficient with rising salt concentration was determined and assumed to apply in other cases where the anion was not unreactive.

Although the accuracy attained in the present work is not as high as that of Brønsted *et al.*, largely because only limited quantities of the diepoxides were available, they are more satisfactory in that no assumptions were made regarding the rate coefficient for the reaction with water. As in the case of reaction with the thiosulphate ion, it was necessary to prevent the solution becoming alkaline because of reaction (3), and this was done by having an excess of acetic acid present; the buffering action of sodium acetate kept the pH of the solution within the required limits. The amount of ester formed was determined as in the experiments of Brønsted *et al.* by titrating the remaining acetic acid, and the epoxide content of the solution was determined in the same aliquot, after addition of acetone, by the thiosulphate method. As the acetic acid is little dissociated, practically all the acetate ions come from the sodium acetate, and as the oxide reacts by equation (3) the acid is neutralised, with the result that the acetate-ion concentration is kept constant. Thus for the reaction with water (1):

$$\mathrm{d[oxide]}/\mathrm{d}t = k_1[\mathrm{oxide}] \quad . \quad . \quad .

TABLE III.

Reaction of epoxides in aqueous solutions containing 0·1N-acetic acid and various concentrations of sodium acetate. (Concn. of oxide, 0·1M. for monoepoxides and 0·05M. for dieposides. Temp., 37°. Time, 24 hours.)

NaOAc, M.	% ester formed.	% glycol formed.	% epoxide reacting.	k_1.	k' (Ac).	k_2 (Ac).
Epichlorohydrin.						
0	—	36·5	36·5	0·019	—	—
0·1	20·6	31·4	52·0	0·0185	0·012	0·12
0·2	34·5	28·0	62·5	0·0185	0·023	0·115
0·5	59·8	21·7	81·5	0·019	0·052	0·104
1·0	77·3	16·9	94·2	0·021	0·098	0·098
Glycidol.						
0	—	15·6	15·6	0·0071	—	—
0·1	7·8	15·0	22·8	0·0075	0·0036	0·036
0·2	13·5	15·3	28·8	0·0076	0·0066	0·033
0·5	27·3	14·7	42·0	0·0080	0·0150	0·030
1·0	44·8	14·2	59·0	0·0089	0·028	0·028
1 : 2-3 : 4-*Diepoxybutane.*						
0	—	15·5	15·5	0·0070	—	—
0·1	11·1	15·2	26·3	0·0074	0·0055	0·055
0·2	19·7	14·7	34·4	0·0075	0·0101	0·050
0·5	38·4	12·2	50·6	0·0071	0·0225	0·045
1·0	58·5	10·5	69·0	0·0074	0·041	0·041
1 : 2-5 : 6-*Diepoxyhexane.*						
0	—	42·0	42·0	0·023	—	—
0·1	6·05	64·95	71·0	0·047	0·0044	0·044
0·2	11·0	57·8	68·8	0·041	0·0078	0·039
0·5	20·6	50·0	70·6	0·036	0·0150	0·030
1·0	33·4	44·2	77·6	0·036	0·027	0·027
Di*-(2 : 3-*epoxypropyl*) *ether.						
0	—	15·5	15·5	0·0071	—	—
0·1	6·6	15·2	21·8	0·0071	0·0031	0·031
0·2	12·6	15·9	28·5	0·0078	0·0087	0·031
0·5	28·8	16·2	45·5	0·0090	0·0161	0·032
1·0	47·6	14·4	62·0	0·0094	0·031	0·031

TABLE IV.

Reaction of* 1 : 2-3 : 4-*diepoxybutane with various anions. (Concn. of epoxide, 0·025M. Temp., 37°. Time, 24 hours.)

Anion.	% ester formed.	% epoxide reacting.	% conversion into ester.
1. 0·25M-Thiosulphate, 0·05N-acetic acid	100	100	100
1a. 0·025M-Thiosulphate, 0·05N-acetic acid	92·5	98	94·5
2. 0·5M-Iodide, 0·05N-acetic acid	97	100	97
3. 0·166M-Citrate, 0·05N-citric acid	47·2	57·7	82·5
4. 0·5M-Chloride, 0·05N-acetic acid	53	66	80·3
5. 0·5M-Acetate, 0·05N-acetic acid	38·4	50·9	75·5
6. 0·5M-Benzoate, 0·05N-benzoic acid	30·1	45·8	65·6
7. 0·25M-Tartrate, 0·05N-tartaric acid	23·7	40·7	58·1
8. 0·25M-Oxalate, 0·05N-oxalic acid	31	54·7	56·6
9. 0·5M-Formate, 0·05N-formic acid	20·2	64·85	31·2
10. 0·5M-Nitrate, 0·05N-acetic acid	2·5	32	7·6
11. 0·5M-Acetate	3·6	50·7	
12. 0·5M-Benzoate	6·0	44·5	
13. 0·5M-Chloride	2·5	27·5	
14. 0·25M-Thiosulphate	21·8	68	
15. 0·00125N-Sodium hydroxide	—	15·7	
16. 0·1N-Sodium hydroxide	—	85	
17. 0·5N-Sodium hydroxide	—	100	
18. Water alone	—	15·5	
19. 0·05N-Acetic acid	nil	30·0	

TABLE V.

Compound.	k_2.[a]	k_2 (Ac).[a]	k′ (thio).[b]	k′ (thio).[c]
Glycidol	0·0069	0·036	1·15	0·90
Epichlorohydrin	0·0155	0·12	1·50	1·12
1 : 2-3 : 4-Diepoxybutane	0·0075—0·0050	0·055—0·033	0·85	0·67
Di-(2 : 3-epoxypropyl) ether	0·0068	0·033	0·69	0·55
1 : 2-5 : 6-Diepoxyhexane	0·023	0·043	0·40	0·34

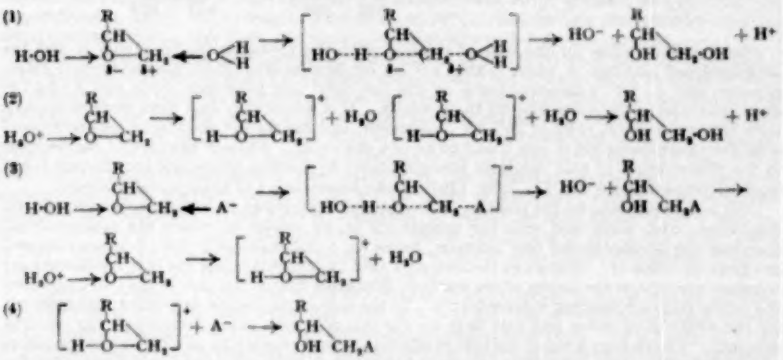
[a] From Table II. [b] From Table I. [c] The conditions were exactly as described for results in Table I except that 0·2M-sodium acetate was also present.

TABLE VI.

Rate coefficient (k_2) *for the acid-catalysed addition of water* (for conditions, see p. 2271).

Compound.	k_2 (at pH = 7).	k^3 (at pH = 3).	k^1 (at pH = 1).	Average value of k_2.
Propylene oxide	0·0091	0·495	40·5	—
$k_2 = k^3 - k_1/[H^+]$	—	484	405	445
Glycidol	0·0071	0·050	4·75	—
k_2	—	43	47	45
Epichlorohydrin	0·019	0·026	0·71	—
k_2	—	7·0	6·9	6·95
1 : 2-3 : 4-Diepoxybutane	0·0070	0·0143	0·68	—
k_2	—	7·3	6·7	7·0
1 : 2-5 : 6-Diepoxyhexane	0·023	0·66	64·0	—
k_2	—	637	640	639
Di-(2 : 3-epoxypropyl) ether	0·0070	0·216	2·17	—
k_1	—	24·6	21·6	23·1
Methiodide of *NN*-di-(2 : 3-epoxypropyl)-*p*-anisidine	0·0073	—	0·0304	—
k_2	—	—	0·23	0·23
2 : 4 : 6-Tri(ethyleneimino)-1 : 3 : 5-triazine	0·024	30·0	—	—
k_2	—	$2·98 \times 10^4$	—	$2·98 \times 10^4$

under conditions where "spontaneous" and acid-catalysed reaction can occur are best explained by considering that the following mechanisms operate for the reactions (1)—(4) on p. 2258.



The unstable oxiran ring will be partly polarised with a fractional negative charge on the oxygen atom and a similar positive charge on the terminal carbon atom. The direction of ring fission shown in this scheme applies to those compounds where R is an electron-attracting group (see below). Spontaneous addition of water (1) is regarded as an attack on the positively-charged carbon atom by a water molecule acting as a base by reason of the lone pair of electrons on its oxygen atom, followed by solvation of the charged oxygen atom and subsequent elimination of hydrogen and hydroxyl ions in equivalent amounts so that the solution remains neutral. Similarly, the reaction with an anion (3) involves the attack of the carbon atom by the anion followed by solvation of the charged oxygen atom. In this instance hydroxyl ions alone are eliminated and the solution becomes alkaline. In the acid-catalysed reactions (2) and (4) the two stages are considered to be the attack of the hydrogen—or more likely the oxonium—

ion on the oxygen atom yielding an acid complex followed by the attack of the base (anion or water molecule) on the carbon atom.

It is now suggested that the initial step in the spontaneous reactions is the attack of the base on the terminal carbon atom but in the acid-catalysed reaction it is the attack of the oxygen atom by the oxonium ion. The dependence of the rate of the spontaneous reaction upon the concentration of base (Table III) and its independence of hydrogen-ion concentration over a wide range, and the dependence of the rate of the acid-catalysed reaction upon the hydrogen-ion concentration (Table VI) seem to support this view.

If these mechanisms are correct it would be expected that substituents in R which are electron-attracting and which tend to increase the positive charge on the terminal carbon atom and decrease the negative charge on the oxygen atom would favour reactions (1) and (3) and retard reactions (2) and (4).

The effect of electron-attracting groups such as $\geqslant\overset{+}{N}\cdot CH_2^-$, $Cl\cdot CH_2^-$, and $HO\cdot CH_2^-$ on the velocity of reaction with the thiosulphate anion, shown in Table I, support the proposed mechanism. As would be expected, the positively-charged nitrogen atom in the quaternary compound causes by far the greatest increase in reaction rate. Electron-repelling groups such as CH_3^-, $CH_3\cdot CH^-$, and $R_2N\cdot CH_2^-$ decrease the reactivity towards anions in neutral solutions. If both carbon atoms of the epoxide ring are substituted by such groups a large diminution of reactivity results as in the case of the oxides of *cyclo*hexene, limonene, and dihydromyrcene. The high reactivity of **1 : 2-3 : 4-diepoxybutane** is probably due to the fact that when one epoxide ring has reacted the product has a glycidol-like structure (inset), and the second ring will react more readily, leading to a higher overall reaction rate.

$CH_2A\cdot CH(OH)\cdot CH\cdot CH_2$ (O)

Conversely, electron-attracting groups should decrease the rate of acid-catalysed reactions by lowering the effective negative charge on the oxygen atom; in fact, substituents should have an opposite effect on the two types of reaction. That this is so is clearly shown by the results of Brønsted *et al.* (*loc. cit.*), who found the following rate coefficients for ethylene oxide and epichlorohydrin at 20°:

	Ethylene oxide.	Epichlorohydrin.
k_3	$3{\cdot}6 \times 10^{-7}$	$9{\cdot}7 \times 10^{-7}$
k_2	$5{\cdot}33 \times 10^{-4}$	$0{\cdot}41 \times 10^{-4}$

The relative values for the rate of reaction with the thiosulphate ion (Table I) and the acid-catalysed addition of water (Table VI) for epichlorohydrin, di-(**2 : 3**-epoxypropyl) ether, glycidol, and **1 : 2-3 : 4**-diepoxybutane on the one hand and propylene oxide and **1 : 2-5 : 6**-diepoxyhexane on the other support these results. It is noteworthy that these workers found a very high value for k_2 (1·92 at 20°) for *cyclo*hexene, and the rate of reaction of this compound with the thiosulphate ion is now found to be of a low order. Another example of the decrease in the effectiveness of acid catalysts brought about by electron-attracting substituents is the work of Watson and Yates (*J.*, 1932, 1207) on the bromination of halogenated acetones.

The rate coefficients for the reaction of several typical epoxides, including three radiomimetic diepoxides, with water and with the acetate ion under conditions where the acid-catalysed reactions can be disregarded (see, however, below for a discussion of **1 : 2-5 : 6**-diepoxyhexane) are given in Table II. Except in the case of **1 : 2-3 : 4**-diepoxybutane the rate coefficients are constant throughout the course of the reaction, indicating that in the case of the two diepoxides the oxiran rings are reacting independently. In the case of the butane derivative the coefficient for the addition of water and also that for the reaction with anion decrease as the reaction proceeds. The slowing down of the rate of addition of water cannot be ascribed to the formation of a glycidol-like compound since glycidol reacts at the same rate as the initial value for the diepoxide, but it is interesting to note that the coefficient for the reaction of the butane compound with acetate ions gradually falls to the value for glycidol.

The rate of addition of water to **1 : 2-5 : 6**-diepoxyhexane in 50% acetone is much less than in water alone, but there is not a proportional drop in the rate of reaction with the acetate ion, with the result that considerably more ester is formed when the reaction proceeds in aqueous acetone.

The value of the rate coefficient for the addition of water (k_1) with increasing salt concentration (Table III) is practically constant in the case of epichlorohydrin and **1 : 2-3 : 4**-diepoxybutane, but rises in the case of glycidol and di-(**2 : 3**-epoxypropyl) ether. Brønsted *et al.* (*loc. cit.*) described this positive salt effect: our own experiments were only accurate enough to detect large changes. The values of the coefficient k_2 are tolerably constant—the decrease in most

cases can probably be ascribed to incomplete ionisation of the sodium acetate at higher concentrations. The values for 1 : 2-5 : 6-diepoxyhexane are again abnormal, but these can be accounted for (see below).

The various coefficients determined in this study are collected in Table V. The rate coefficients for reaction with acetate and thiosulphate anions are in the same order for epichlorohydrin, 1 : 2-3 : 4-diepoxybutane, and di-(2 : 3-epoxypropyl) ether, but there is a divergence in the case of glycidol and 1 : 2-5 : 6-diepoxyhexane. Close correlation in the coefficients could hardly be expected since the values for acetate were determined in aqueous solution, and although an excess of acetic acid was always present, the buffering action of the acetate ions meant that the pH never fell below about 4·5; the thiosulphate values —k'(thio)— were determined in 50% acetone and the pH of the solution was probably lower, for although only small additions of acetic acid were made, the thiosulphate ion has no buffering action. The effect of this acidity would be expected to be most marked in the case of the more rapidly reacting oxides for with these it is necessary to follow the reaction by adding an excess of acetic acid and timing the reappearance of the phenolphthalein colour after each addition: the reaction is too rapid to follow by a continous titration as can be done with the less reactive compounds. Any appreciable change in pH can be prevented by the addition of sodium acetate to the thiosulphate solution—the rate coefficient for the reaction with the acetate ions alone was negligible [k'(Ac) $<$ 0·002 in boiling 50% acetone]. Some values for the rate coefficients in buffered thiosulphate are given in Table V. It will be seen that the rate of reaction is always lowered to some extent if the pH is kept nearer neutrality, but the reactivity of glycidol towards thiosulphate is still high as compared with its reactivity to acetate ions.

The reactions of 1 : 2-5 : 6-diepoxyhexane in aqueous solution are known to be abnormal. Wood and Wiggins (*Nature*, 1949, **164**, 402) have shown that when the compound is boiled with water, 2 : 5-di(hydroxymethyl)furan is formed in 65% yield. This furan derivative has now been obtained in good yield by allowing the diepoxide to react in dilute hydrochloric acid. Another unusual feature is the low yield of ester when 1 : 2-5 : 6-diepoxyhexane reacts in 0·1M-sodium acetate solution. Only about 8% of the reacting oxide is converted into ester, whereas the yields of ester in other cases are: epichlorohydrin, 40%; glycidol, 34%; 1 : 2-3 : 4-diepoxybutane, 38%; di-(2 : 3-epoxypropyl) ether, 33%. Despite this low yield of ester in dilute acetate solution, this diepoxide reacts quantitatively with 0·2M-thiosulphate.

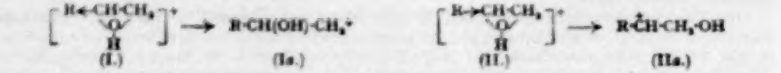
There is an abnormally large increase in the value of k_1 (Table II) when reaction takes place in 0·1M-sodium acetate containing 0·1M-acetic acid—from 0·023 in water alone to 0·046 hr.$^{-1}$ in acetate–acetic acid solution. This increase is not due to a large salt effect, but has been traced to a high value for the rate coefficient of the acid-catalysed reaction (k_2) (Table VI).

As a consequence of the high value of k_2 for 1 : 2-5 : 6-diepoxyhexane, a small increase in acidity will cause a much larger increase in the rate of glycol formation than in the case of the other oxides studied, which have a lower value of k_2. In particular, at the pH of the sodium acetate–acetic acid mixture—found to be 4·6 by direct measurement with a glass electrode system—the coefficient for the rate of formation of glycol by acid catalysis, $k^{4\cdot6}$, will be 640 $\times$ $10^{-4\cdot6}$ or 0·016. The overall rate coefficient for the production of glycol will be $k_1 + k^{4\cdot6}$ or 0·39; thus it can be seen that the increase in the rate of acid-catalysed addition of water accounts for most of the increase observed in Table II.

It was noted that in those cases where the amount of ester formed in dilute acetate solution was between 30 and 40%, and where the value of k_2 was low, the epoxide contained a system which tended to attract electrons away from the terminal carbon atom. In the case of 1 : 2-5 : 6-diepoxyhexane the mutual effect of the two epoxide groups is likely to be small since they are separated by two carbon atoms, in contrast with the system in the butane derivative (see above), and the system approximates to that found in propylene oxide where the tendency would be for electrons to be repelled towards the terminal carbon atom. In fact when the reactions of propylene oxide were studied they were found to have much in common with those of the hexane derivative. The value of k_1 for propylene oxide was 0·008, k_1 in 0·1M-acetate–0·1M-acetic acid was 0·024, k_2(Ac) was 0·040, k_2 was 445, and the values in Table I are of the same order. Only 16% of the epoxide reacting in 0·2M-sodium acetate solution was converted into ester.

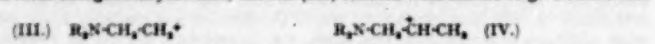
Kadesch (*J. Amer. Chem. Soc.*, 1946, **68**, 41) and Swern, Billen, and Knight (*ibid.*, 1949, **71**, 1152) have discussed the direction of ring fission during the reactions of epoxides under conditions of acid and alkali catalysis. They conclude that, when the group R is electron-attracting, cleavage in the conjugate acid formed during the acid-catalysed reaction will occur

almost exclusively as in (I), whereas if the group is electron-repelling, a considerable proportion of the ring fission will be as in (II):



(I.) (Ia.) (II.) (IIa.)

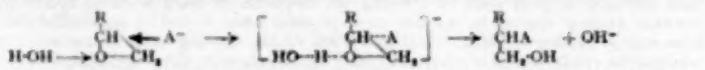
The carbonium ions (Ia) and (IIa) can be regarded as intermediates in the acid-catalysed reactions. It was shown by Everett and Ross (*J.*, 1949, 1972) that, of the carbonium ions (III) and (IV) derived from halogenoalkylamines, the ion (III) reacted with anions to give about four



(III.) (IV.)

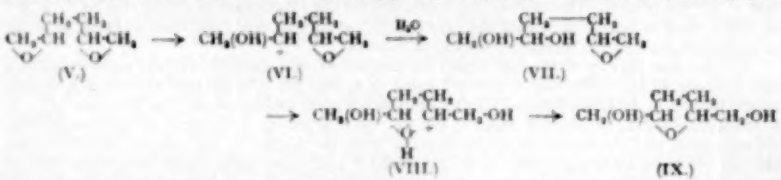
times the yield of ester afforded by the ion (IV). The yields of ester in the reaction of various epoxides with 0·1N-hydrochloric acid (under the conditions given in Table VI) are as follows: epichlorohydrin, 35·5%; 1 : 2-3 : 4-diepoxybutane, 32%; di-(2 : 3-epoxypropyl) ether, 27·6%; glycidol, 25·4%; propylene oxide, 17%; 1 : 2-5 : 6-diepoxyhexane, 9%. Should the abilities of the ions (Ia) and (IIa) to react with anions be similar to those of (III) and (IV), respectively, these figures would indicate that very approximately one-half of the propylene oxide molecules undergo ring fission to give an ion of type (IIa) whilst the remainder give (Ia). This ratio of products is found in the reaction of propylene oxide with ethanol in the presence of 1·3% sulphuric acid (Chitwood and Freure, *J. Amer. Chem. Soc.*, 1946, **68**, 680; see also Reeve and Sadle, *ibid.*, 1950, **72**, 125).

The yields of ester when the various epoxides react in almost neutral solutions of acetate ions (p. 2265) are of the same order as for the acid-catalysed reaction above; this suggests that the initial step in the spontaneous reactions of epoxides where R is electron-repelling involves an attack by the anion on the non-terminal carbon atom, thus:



Chitwood and Freure (*loc. cit.*) have shown that when propylene oxide reacts with ethanol in the absence of a catalyst, ring fission still occurs in both directions, though a higher proportion opens as in (I). In the case of 1 : 2-epoxy-2-methylpropane, which has two electron-repelling methyl groups attached to the same carbon atom, the uncatalysed reaction with methanol and propan-1-ol gives equal yields of primary and secondary ethers, while the reaction with ethanol gives twice as much primary as secondary ether (Sparks and Nelson, *J. Amer. Chem. Soc.*, 1936, **58**, 671).

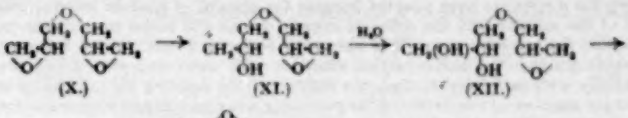
The formation of a furan derivative from 1 : 2-5 : 6-diepoxyhexane and the non-formation of a dioxan derivative from di-(2 : 3-epoxypropyl) ether in their reactions in aqueous solution can also be explained as follows: the first stage in the reaction of the hexane derivative (V) in acid solution will be the formation of the monoglycol (VII) by way of the ion (VI). The conjugate



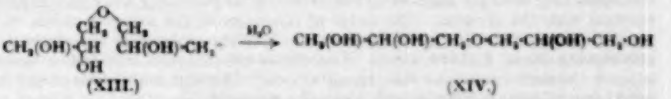
(V.) (VI.) (VII.) (VIII.) (IX.)

acid from (VII) will yield the ion (VIII) which can readily react internally to form the stable five-membered furan ring system (IX). By analogy with the reaction of propylene oxide, about 16% of the ion (VI) should react to form ester in 0·1M-acetate solution but the ion corresponding to (VIII) would probably have a greater tendency to react internally; this would account for the low overall yield of ester. If the ion (VIII) only reacts internally, the overall yield of ester will be about 8%—this is the amount actually formed. When the reaction is carried out in the presence of the highly competing thiosulphate ion, the reaction of the two carbonium ions (VI) and (VIII) with water or the hydroxyl group will be suppressed and no furan will be formed—the reaction with this anion is quantitative.

Di-(2 : 3-epoxypropyl) ether (X) will yield an ion of type (Ia), that is (XI), which gives a monoglycol (XII). This will give an ion (XIII) which cannot react to give a dioxan derivative but affords the tetrol (XIV). Confirmation of the suggested direction of ring opening in the case of this ether is afforded by the high yield of ester in dilute acetate solution, comparable with that of epichlorohydrin and glycidol.



(X.) (XI.) (XII.)



(XIII.) (XIV.)

The pure 1 : 2-5 : 6-diepoxyhexane (b. p. 187—188°) used in this work was prepared by Professor G. A. R. Kon and Mr. J. L. Everett by the oxidation of diallyl with perbenzoic acid (compare Wood and Wiggins, *loc. cit.*). The material obtained by Przybytek (*Ber.*, 1885, **18**, 1352) from the corresponding dichlorohydrin doubtless consists mainly of this diepoxide, although its b. p. is somewhat lower (179—180°). The product of b. p. 153° obtained by the action of sodium on epichlorohydrin (Bigot, *Ann. Chim. Phys.*, 1891, **22**, 433) has also been described as 1 : 2-5 : 6-diepoxyhexane. When this compound (kindly supplied by Professor J. B. Speakman) was examined for reactivity towards the thiosulphate ion under the standard conditions of Table I, it was found to contain only one epoxide group—as might have been expected since it only reacts with one molecule of water and one molecule of hydrogen halide (Bigot, *loc. cit.*)—and this oxiran ring had a higher reactivity towards thiosulphate ions than those of the genuine compound. The value of k'(thio) was close to that of compounds containing the system $-O\cdot CH_2\cdot CH\cdot CH_2-$ (O).

It has been suggested above that in the reaction with anions the opening of the oxiran ring in the case of compounds in which R is electron-attracting occurs exclusively in a direction resulting in the formation of an ester of a primary alcohol. That this is true for 1 : 2-3 : 4-diepoxybutane has been verified as follows: the diepoxide was allowed to react with a concentrated solution of sodium benzoate to which benzoic acid was added as the solution became alkaline to phenolphthalein. The product was resolved by fractional crystallisation into a dibenzoate, m. p. 148°, and a residue of lower melting point which had the same composition. The higher-

$$CH_2(OBz)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OBz \quad \text{(XVI.)}$$

melting ester was shown to be identical with *meso*-erythritol 1 : 4-dibenzoate (XVI) (Ohle and Melkonian, *Ber.*, 1941, **74**, 292) by conversion into the known tetrabenzoate and by oxidation with lead tetra-acetate to the benzoate of glycollaldehyde—identified as its 2 : 4-dinitrophenylhydrazone.

When the low-melting residue was similarly oxidised, practically the same yield of 2 : 4-dinitrophenylhydrazone was obtained; this indicates that the reaction of the dioxide yields almost exclusively a product with the benzoate groups on the terminal carbon atoms—the mixture must contain D-, L-, and *meso*-erythritol 1 : 4-dibenzoates.

The direction of ring opening in the reaction of propylene oxide with benzoate ions has also been examined. The product obtained was treated with toluene-*p*-sulphonyl chloride, giving a mixture similar to that obtained by Chapman and Owen (*J.*, 1950, 579) by benzoylation of the product of reaction between propylene oxide and toluene-*p*-sulphonic acid. Fractional crystallisation of this mixture gave 2-toluene-*p*-sulphonyloxypropyl 1-benzoate—also obtained after treating the mixture with potassium thiolacetate (Chapman and Owen, *loc. cit.*)—and 2-benzoyloxypropyl 1-toluene-*p*-sulphonate.* Thus, contrary to the statement of Fraenkel-Conrat and Olcott (*J. Amer. Chem. Soc.*, 1944, **66**, 1420), when propylene oxide reacts with anions ring fission occurs with the formation of both isomeric hydroxy-esters. An attempt to estimate the relative proportions of the two esters formed in the reaction with sodium iodide

* The author is indebted to Dr. L. N. Owen and Mr. G. A. Haggis for advice on the separation of these esters and for a specimen of 2-benzoyloxypropyl 1-toluene-*p*-sulphonate (Haggis and Owen, *J.*, 1950, 2250).

in acetone at 100° (Oldham and Rutherford, *J. Amer. Chem. Soc.*, 1932, **54**, 366) was unsuccessful since both isomers reacted quantitatively under these conditions.

Table IV shows the extent of the reaction of the physiologically active 1 : 2-3 : 4-diepoxybutane with various anions under comparable conditions. The figures given in the final column represent the percentage of the reacting epoxide which has been converted into ester. This method of expressing the results has been adopted because the amount of epoxide reacting will depend on the pH of the solution and the different organic anions will buffer the solution to different extents, whilst the inorganic anions will have little buffering action. Since Brønsted *et al.* (*loc. cit.*) have shown that the acid-catalysed reactions with water and with anions are increased proportionally with increasing acidity, the fraction of the reacting epoxide which is converted into ester is a measure of the ability of the particular anion to compete with water for reaction with the epoxide. The order of reactivity of the anions towards the oxiran ring is similar to that found for their reactivity towards the carbonium ions derived from halogenoalkylamines (Ross, *J.*, 1949, 2589). The nitrate ion competes only feebly, and the formate ion is again the least reactive of the organic anions. The high reactivities of the thiosulphate and iodide ions is also common to both types of compound.

If no acid is present (11—14, Table IV) the solution soon becomes alkaline owing to reaction (3) (p. 2258); under these conditions considerably less ester is formed in the presence of acetate, benzoate, and chloride ions and appreciably less in the case of the thiosulphate ion. Although less ester is formed in the reaction with acetate and benzoate ions in the absence of added acid, the total amount of epoxide reacting is practically the same (compare 5 and 11, and 6 and 12, Table IV). The increase in alkalinity in the case of the reaction with the acetate ion results in the solution becoming 0·00125N. with respect to hydroxyl ions. That this increase in pH—to 11·7—is not responsible for the increased amount of epoxide reacting is shown in the table (compare 15 and 18). Since the amount of epoxide reacting is dependent on the anion concentration, although little ester is formed, and as it has been shown that there is no significant increase in the rate of reaction with water with increasing anion concentration (Table III), it appears that the reaction proceeds by the initial formation of an ester which is subsequently hydrolysed.

In the reactions with chloride and thiosulphate ions less epoxide is transformed than when acid is present, though more reacts than in the absence of the anion. It seems likely that esters are again the primary products, but this time the increase in pH probably causes a reversal of the reaction and an equilibrium state is reached. The conversion of 1-chloro-2-hydroxypropane into propylene oxide in 76—84% yield by treatment with N/40-sodium hydroxide at 37° shows that the reaction is reversible under the mild conditions used to obtain the results given in Table IV.

When the concentration of hydroxyl ions is increased to 0·10M. there is a considerable increase in the amount of epoxide reacting, and when the concentration is 0·5M.—comparable to the concentration of the other anions in Table IV—all the epoxide is transformed. Thus, contrary to the statement of Brønsted *et al.* (*loc. cit.*) which is discussed by Hammett ("Physical Organic Chemistry," New York, 1940, p. 301), it appears that the hydroxyl ion does react with an epoxide ring system, the rate of reaction being faster than with chloride, acetate, and nitrate ions. This increase in the rate of conversion of epoxides into glycols in the presence of 0·1M-hydroxyl ions is quite general (see Table VII). The reaction of epichlorohydrin with hydroxyl ions could not be studied because the chlorine atom is rapidly hydrolysed in 0·1N-sodium hydroxide. Ogston (*loc. cit.*) also found that hydroxyl ions were able to react more readily than chloride and acetate ions with the carbonium ions derived from di(chloroethyl) sulphide.

TABLE VII.

Time of reaction, 24 hours. Temp., 37°. Concn. of monoepoxide, 0·1M.; of diepoxide, 0·05M.

Compound.	% reacting in water.	% reacting in 0·1N-NaOH.
Ethylene oxide	18·4	94·5
Propylene oxide	16·3	92·5
Glycidol	15·6	88
1 : 2-3 : 4-Diepoxybutane	15·5	85
Di-(2 : 3-epoxypropyl) ether	15·5	98

A first-order rate function being assumed with respect to each reactant the unimolecular constant for the reaction of an epoxide in mixed aqueous solution can be represented as

$$k = k_1 + k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_{A^-}[A^-]$$

This is of the same form as the equation for an acid–base-catalysed reaction. Approximate values for the various constants on the right-hand side of this equation can be deduced for several epoxides from the figures in Tables V, VI, and VII; they are collected together in Table VIII.

TABLE VIII.

Rate coefficients for the reactions of epoxides in aqueous solution.

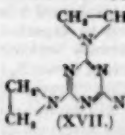
Compound.	$k_1 \times 10^5$.	k_2.	k_{OH}.	$k_2(Ac) \times 10^5$.
Glycidol	6·9	45	0·82	3·6
Propylene oxide	8	445	0·99	5
Epichlorohydrin	18·5	7	—	12
Di-(2 : 3-epoxypropyl) ether	6·8	23	*ca.* 1·6	3·3

Unsaturated compounds containing an electron-attracting group adjacent to the ethylenic linkage would also be expected to react with nucleophilic reagents owing to the polarisation induced by the displacement of the π-electrons. When divinyl sulphone, acraldehyde, and acrylonitrile are heated with aqueous acetone solutions of thiosulphate under the conditions described in Table I, alkalinity is developed at a measurable rate. The reaction of divinyl sulphone with thiosulphate was previously observed by Stahman, Golumbic, Stein, and Fruton (*J. Org. Chem.*, 1946, **11**, 719). This reaction can also be regarded as proceeding by the Lowry mechanism, the attack on the polarised double bond being as follows:

$$H{-}O{-}H \longrightarrow {}^{\delta-}\!\left[\begin{matrix} R \\ | \\ CH{=}CH_2 \end{matrix}\right]^{\delta+} \longleftarrow A^- \longrightarrow R{\cdot}CH(OH){\cdot}CH_2A + OH^-$$

The rate of reaction of divinyl sulphone is comparable with that of the biologically active diepoxides and, although it has proved to be too toxic to be of value as a tumour-growth inhibitor, it does produce chromosome abnormalities in the growing root tips of *Vicia faba* similar to those obtained with other difunctional electrophilic reagents (personal communication from Mr. A. Loveless).

Another type of compound examined which reacts in a manner very like that of the diepoxides is the 2 : 4 : 6-triethyleneimino-derivative of 1 : 3 : 5-triazine (XVII). Like several diepoxides, this substance has been used as a cross-linking agent in the textile industry (Preston, "Fibre Science," Manchester, 1949, p. 266). Since it reacts with wool fibres under quite mild conditions—the treatment involves steeping the material for a short time in a 5—10% solution at 60°—the compound was of interest as a potential radiomimetic agent. The rate of reaction of the triazine with water at 37° was of the same order as the effective diepoxides (k_1 for a 24-hour period being 0·023 hr.$^{-1}$) and the rate of reaction with thiosulphate was also comparable (Table I).


(XVII.)

The yield of ester in acetate solutions under the conditions described in Table II was 26% (compare p. 2264) and the yield of chloride in the reaction with 0·1N-hydrochloric acid was 42%—slightly higher than for most epoxides. The only significant respect in which the triazine differs from the epoxides is in the very high value of the coefficient for the rate of the acid-catalysed reactions (Table VI). In view of these close analogies, it was hardly surprising to find that triethyleneiminotriazine was effective as a tumour-growth inhibitor and in the production of chromosomal derangements (unpublished work by Professor A. Haddow and Mr. A. Loveless).

Table I shows the results of the biological testing of some of the compounds now examined for chemical reactivity. An outstanding feature is the finding that no monofunctional epoxide is effective as a tumour-growth inhibitor. In general, the toxicity of the compounds is proportional to the rate at which the oxiran ring will react with an anion except that a difunctional compound is more toxic than a monofunctional compound of comparable chemical reactivity [compare epichlorohydrin and glycidol with 1 : 2-3 : 4-diepoxybutane and di-(2 : 3-epoxypropyl) ether; and also propylene oxide with 1 : 2-5 : 6-diepoxyhexane]. This is paralleled in the mustard-gas types of compound; for example, ethyl 2-chloroethyl sulphide and dimethyl-2-chloroethylamine are much less toxic than di-2-chloroethyl sulphide and methyldi-2-chloroethylamine respectively. Even amongst the diepoxides it would appear that a certain minimum reactivity—as measured by the rate of reaction with the thiosulphate ion—must be exceeded before the compound is growth-inhibitory, though this level of reactivity is not, in itself, sufficient for activity. The methiodide of *NN*-di-(2 : 3-epoxypropyl)-*p*-anisidine is not active,

nor is the ester of di-(2 : 3-epoxypropyl)acetic acid—the latter is probably hydrolysed in the tissues to give a carboxylate anion in which the epoxide groups would be less reactive on account of the negative charge. These two exceptions yield ions, and since these compounds probably have to diffuse into the cell to exert their effect, they may be inactive because of an inability to penetrate the cell membrane (compare Seligman, Friedman, and Rutenburg, *Cancer*, 1950, **3**, 342). Grove and MacGowen (*Chem. and Ind.*, 1949, 647) give an account of a series of fungicides in which ions are inactive because of an inability to penetrate cells. The inactivity of the epoxypropyl derivatives of quinol and resorcinol is unexpected, but since these compounds have a much lower water and lipoid solubility than the other simple diepoxides, it may be that a sufficient concentration of the agents cannot be attained at the required site of action. The high-melting isomer of *p*-di-(2 : 3-epoxypropoxy)benzene only exerts a transient effect upon the growth of the transplanted Walker tumour; it is not as active as the simpler diepoxides.

The substitution of both carbon atoms of the oxiran rings reduces the reactivity below that required and hence it would not seem worth investigating other compounds of this type. There are, however, indications that, although two reactive centres are required in the molecule, these centres need not be equally reactive; for example, the effective 1 : 2-3 : 4-diepoxy-2-methylbutane must contain centres of unequal reactivity. Another example is *N*-2-chloroethyl-*N*-3-chloropropylaniline (Kon and Roberts, *J.*, 1950, 978) which is a growth-inhibitor though the corresponding di-(3-chloropropyl) derivative is ineffective. These results suggest that only one group of high chemical reactivity is required—this would anchor the molecule to a receptor and the second group would then have more time to combine with another receptor (compare Goldacre, Loveless, and Ross, *Nature*, 1949, **163**, 667).

The high rate coefficient for the acid-catalysed reactions of certain diepoxides, such as 1 : 2-5 : 6-diepoxyhexane is of considerable interest, for it explains why this compound is ineffective when administered by mouth. It can be calculated that, at the pH of the stomach, over 90% of this oxide is decomposed within two minutes. It would be expected that this type of compound would react more readily with nucleophilic centres (see p. 2268) in regions where the acidity is relatively higher; this might be significant from the standpoint of selective action towards different tissues.

Fraenkel-Conrat (*J. Biol. Chem.*, 1944, **154**, 227) has shown, and the present study confirms, that epoxides react readily with ionised acid groups, but not with undissociated acids, and it is also known that they react with free amino-groups. These characteristics are to be expected if the epoxides react through a carbonium-ion mechanism. An important difference between the epoxides and the mustard-gas type of compound is that, whereas the latter react by an S_N1 mechanism and the extent of reaction is largely independent of the concentration of reacting centres, the former react by a bimolecular mechanism and the extent of reaction will depend on the availability of reacting centres. This is probably of some importance in the reactions of epoxides with biological systems where the concentration of reacting groups will vary from site to site. Nucleic acids contain a high proportion of ionised phosphate groups and so reaction with epoxides would be specially favoured.

It has been pointed out (Ross, *J.*, 1950, 815) that agents reacting by a carbonium-ion mechanism will be capable of reacting with free amino-groups and with ionised thiol groups as well as with anions. Since compounds, such as di-acid chlorides, diisocyanates, and di-iodoacetyl derivatives of diamines * and of diphenols, which would be expected to react with amino- and thiol groups but not with acidic groups, do not inhibit the growth of the Walker tumour (unpublished work by Professor A. Haddow), nor do they produce chromosomal abnormalities in the growing root tip of *Vicia faba* (Mr. A. Loveless, in the press), one is led to the conclusion that the various radiomimetic compounds owe their especial properties to an ability to react with ionised acidic groupings under mild conditions.

Experimental.

Determination of Epoxides with Thiosulphate.—When an epoxide is heated in a solution of sodium thiosulphate in 50% acetone, the solution rapidly becomes alkaline. It has been shown that the reaction producing hydroxyl ions (reaction 3, p. 2268) is quantitative, provided that the solution is kept almost neutral by titration with a weak acid. Satisfactory results were obtained with the more rapidly reacting epoxides if acetic acid was added before the heating and the excess was titrated after reaction was

* The production of chromosome aberrations in the epithelial cells of the newt, *Triturus palmatus*, by the action of *NN*-di(iodoacetyl)-*o*-phenylenediamine reported previously (*J.*, 1949, 1972) has not been confirmed by later work—the original results remain unexplained (private communication, Mr. A. Loveless).

complete, but this method was unsuitable for the less reactive compounds since the more prolonged heating resulted in the decomposition of the unstable thiosulphuric acid with deposition of sulphur. This decomposition does not occur at 37° in completely aqueous solution. The method finally adopted for the determination of epoxides was as follows: the monoepoxide (1 millimol.) or the diepoxide (0·5 millimol.) was added to a neutralised 0·2N-solution of sodium thiosulphate in 50% acetone containing phenolphthalein, and the mixture was heated in a flask carrying a reflux condenser and a stopper holding a 10-ml. burette. As the solution was heated, the pink colour which developed was continuously discharged by adding 0·2N-acetic acid from the burette. When no further alkalinity was produced—generally after 10—20 minutes—the solution was cooled and any excess of acetic acid titrated with 0·1N-sodium hydroxide (1 ml. of 0·1N-acid = 0·1 milliequiv. of oxiran oxygen). All epoxides of structure R·CH·CH$_2$ gave a quantitative liberation of hydroxyl ions under these conditions.

Determination of k′ *(thio) for Various Epoxides* (Table I).—The conditions were exactly the same as for the determination of epoxides except that the thiosulphate solution was heated to boiling before the epoxide was added in a small sample tube. The solution was continuously titrated with 0·2N-acetic acid and the burette readings were recorded at regular intervals. With the more rapidly reacting epoxides it was found necessary to add a known small amount of acid and then to time the return of the pink colour and so on. A typical experiment was that with 1 : 2-3 : 4-diepoxybutane:

Time, secs.	14	22	30	39	52	67	76	87
% epoxide reacted...	17·9	26·8	35·7	44·6	53·6	62·5	67	71·5
100 k' (thio), min.$^{-1}$	85	85	87	89	87	85	87	87

Time, secs.	104	117	135	160	205	236	∞	
% epoxide reacted...	76	80·4	85	89·5	94	96	100	
100 k' (thio), min.$^{-1}$	85	83	85	85	83	83	—	

Average value: k' (thio) = 85 × 10^{-4} min.$^{-1}$.

Reaction of Epoxides in Water and Aqueous Acetate Solutions (Tables II and III).—The monoepoxide (10 millimols.) or diepoxide (5 millimols.) was dissolved in (*a*) water (100 ml.) or (*b*) 0·1N-acetic acid (100 ml.) containing sodium acetate (1·36 g.) and kept at 37°. Immediately after the mixing, an aliquot (10 ml.) was removed and in (*a*) after addition of an equal volume of acetone and then sodium thiosulphate—to give a 0·2N-solution—the sample was heated and the epoxide content determined as described above; in (*b*) the solution was first titrated with 0·1N-sodium hydroxide, and then the epoxide content was determined as before. The addition of acetone is not essential but its presence prevents the stem of the burette from emptying and the addition of acid is much easier. At suitable intervals similar aliquots of the solution were removed and titrated for epoxide content and acidity. The percentage of ester formed was calculated from the amount of acid neutralised.

The figures given in Table III were obtained in a similar manner by varying the amount of sodium acetate in the solution.

Reaction of 1 : 2-3 : 4-*Diepoxybutane with Different Anions* (Table IV).—1 : 2-3 : 4-Diepoxybutane (86 mg., 1 millimol.) was dissolved in a solution of the appropriate acid (40 ml., 0·05N.) containing the sodium salt (sufficient to give the concentration shown in the table). After the solution had been kept at 37° for 24 hours, the acidity and epoxide content were determined and the amounts of ester formed and epoxide reacting were calculated in the usual manner.

Determination of the Rate Coefficient for the Acid-catalysed Addition of Water (k_3) (Table VI).—The rates of decomposition of an epoxide in water and in 0·05N-acetic acid were determined as above, but for the reaction in 0·1N-hydrochloric acid it was necessary to stop the reaction by rapidly adding sodium hydroxide equivalent to the amount of acid originally present. The excess of alkali was then titrated and the amount of ester formed was calculated; the epoxide remaining was determined on the same aliquot of solution.

Conversion of 1 : 2-5 : 6-*Diepoxyhexane into* 2 : 5-*Di(hydroxymethyl)furan.*—A solution of 1 : 2-5 : 6-diepoxyhexane (2 g.) in 0·1N-hydrochloric acid (50 ml.) was slowly evaporated on a steam-bath. The last traces of water were removed by repeated evaporation with methanol and finally with benzene. The residue was dissolved in pyridine (5 ml.) and, after cooling to 0°, toluene-*p*-sulphonyl chloride (4 g.) was gradually added. Next day the mixture was poured on ice and left for 2 hours. The solid product crystallised from methanol in the form of flattened needles, m. p. 114—117°, not depressed by admixture with material of m. p. 116—118° obtained by the reaction with water alone. Wood and Wiggins (*loc. cit.*) obtained a mixture of di-toluene-*p*-sulphonates of m. p. 114—118° by the action of water.

Methiodide of NN-*Di*-(2 : 3-*epoxypropyl*)-*p*-*anisidine.*—The anisidine (5 g.), dissolved in methyl iodide (10 ml.), was kept at 37° for 24 hours. The sticky solid obtained after rubbing the product with benzene was collected and digested with hot acetone. The resultant colourless solid was crystallised by dissolving it in a small quantity of hot methanol, adding hot acetone, and then cooling slowly. In this way thick plates of the *methiodide*, m. p. 138—139°, were obtained (Found: C, 46·1; H, 5·2; oxiran-O by thiosulphate method, 8·6; I′, 34·9. $C_{16}H_{24}O_3NI$ requires C, 46·3; H, 5·6; oxiran-O, 8·8; I′, 35·0%). The methiodide is soluble in water (20 mg. per ml. at 37°).

Conversion of 1-*Chloropropan*-2-*ol into Propylene Oxide.*—(*a*) The chlorohydrin (131 mg.) was dissolved in 0·025N-sodium hydroxide (40 ml.) and kept at 37° for 17 hours. All the alkali had then been neutralised, showing that 72% of the chlorohydrin had reacted. Titration of the solution by the thiosulphate method indicated the presence of propylene oxide (49 mg.); thus 84% of the chlorohydrin which had reacted was converted into epoxide. (*b*) The chlorohydrin (94·5 mg., 1 millimol.) was similarly heated with 0·025N-sodium hydroxide (40 ml., 1 millimol.) for 24 hours. All the alkali was

neutralised and the solution contained propylene oxide (44 mg.); thus, the whole of the chlorohydrin had reacted and 76% was converted into epoxide.

Reaction of Epoxides in Dilute Sodium Hydroxide Solution.—The monoepoxide (2 millimols.) or diepoxide (1 millimol.) was dissolved in 0·1N-sodium hydroxide (20 ml.) and kept at 37° for 24 hours. After titration of the alkali with 0·2N-acetic acid the epoxide content of the solution was determined in the usual manner. No consumption of alkali was observed in any experiment.

Reaction of 1 : 2-3 : 4-*Diepoxybutane with Benzoate Ions.*—1 : 2-3 : 4-Diepoxybutane (8·6 g.) was dissolved in a solution of sodium benzoate (50 ml., 2N.) containing phenolphthalein. Solid benzoic acid was added to the heated solution at such a rate that the pink colour was continuously discharged. When 20 g. of acid had been added, no further alkalinity developed and the cooled solution was poured into dilute aqueous ammonia. The oil which separated was dried and shaken with benzene, and the solid (6 g.) thus obtained was crystallised from benzene and finally from methanol, giving the dibenzoate as prisms (1·5 g.), m. p. 145—146° (Found: C, 65·6; H, 5·3. Calc. for $C_{18}H_{18}O_4$: C, 65·4; H, 5·5%). Ohle and Melkonian (*loc. cit.*) give m. p. 148° for the 1 : 4-dibenzoate of *meso*-erythritol. Benzoylation of this dibenzoate with an excess of benzoyl chloride in pyridine afforded the tetrabenzoate, needles (from benzene), m. p. 187°; Ohle and Melkonian give m. p. 188—188·5° for *meso*-erythritol tetrabenzoate. The mother-liquors from the original benzene solution were evaporated to dryness, giving a solid (6 g.), m. p. 124—136° (Found: C, 65·7; H, 6·0%).

Oxidation of the Dibenzoate with Lead Tetra-acetate.—The dibenzoate (1 g.) [(i), m. p. 145—146° or (ii), m. p. 124—130°] and lead tetra-acetate (1·35 g.), dissolved in dry benzene (50 ml.), were heated under reflux for 2 hours. The filtered solution was then washed with sodium hydrogen carbonate solution (50 ml.; 2N.) and water, and finally dried (Na_2SO_4) and evaporated. The residue was dissolved in a saturated solution of 2 : 4-dinitrophenylhydrazine in alcohol (70 ml.) and acetic acid (10 ml.). Next day the precipitated dinitrophenylhydrazone was collected: (i) yielded 300 mg. and (ii) 280 mg.—both products melting at 184—185° (Ohle and Melkonian give m. p. 185°). It is realised that the yield is not quantitative but since the mixture (ii) gives the same yield under identical conditions as the purified dibenzoate (i) of known structure it is reasonable to conclude that (ii) contains mainly 1 : 4-dibenzoate.

Reaction of Propylene Oxide with Benzoate Ions.—Propylene oxide was allowed to react in sodium benzoate solution exactly as described above. A solution of the oily product (28 g.) in dry pyridine (100 ml.) was cooled to 0° and treated with toluene-*p*-sulphonyl chloride (40 g.), the temperature being kept below 5°. After 24 hours at room temperature the mixture was poured on ice and the solid product was dried and repeatedly crystallised from light petroleum (b. p. 60—80°). The less soluble fraction—also obtained after treating the mixture with potassium thiolacetate (Chapman and Owen, *loc. cit.*)—formed flattened needles, m. p. 105° (Found: C, 61·1; H, 5·7. Calc. for $C_{17}H_{18}O_5S$: C, 61·1; H, 5·4%), and was identical with the 2-toluene-*p*-sulphonyloxypropyl 1-benzoate prepared by Chapman and Owen. The more soluble fraction, m. p. 77—80°, was extracted several times with ether, and the residue was repeatedly crystallised from light petroleum (b. p. 60—80°), affording fine needles, m. p. 91—92° undepressed by admixture with an authentic specimen of 2-benzoyloxypropyl 1-toluene-*p*-sulphonate, m. p. 93°, kindly supplied by Dr. L. N. Owen and Mr. G. A. Haggis (Found: C, 61·0; H, 5·2%).

*Action of Sodium Iodide on the Isomeric Toluene-*p*-sulphonate-Benzoates of Pro ane-*1 : 2*-diol.*—The ester (2 g.) was heated in a sealed tube at 95—100° for 2 hours with a solution of sodium iodide (2 g.) in acetone (20 ml.). During this time plates of sodium toluene-*p*-sulphonate separated from the solution. The salt was collected, washed with a little acetone, and dried. Yield: from ester, m. p. 105°, 1·17 g.; from ester, m. p. 92°, 1·18 g.; theory, 1·16 g.

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465. *The Action of Sodium Ethoxide on Chroman-4-ones.*

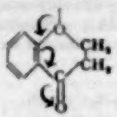
By EILEEN M. PADFIELD and MURIEL L. TOMLINSON.

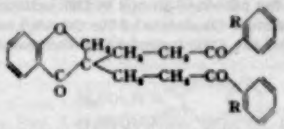
Three crystalline substances have been isolated from the product formed when chroman-4-one is boiled with alcoholic sodium ethoxide. All are polymers of chromanone and there is evidence that one, m. p. 142°, is 3 : 3-di-(2-*o*-hydroxybenzoylethyl)chroman-4-one, formed by interaction of two molecules of *o*-hydroxyphenyl vinyl ketone with one molecule of chromanone. 3 : 3-Di-(2-benzoylethyl)chromanone has been obtained from phenyl vinyl ketone and chromanone, and also from 3 : 3-di-(2-chloroformylethyl)chromanone and benzene. 7-Methoxychroman-4-one is not easily affected by sodium ethoxide, and it has been shown that 2-hydroxy-4-methoxyphenyl vinyl ketone is cyclised by alkali to give 7-methoxychromanone. Preparation of the latter from β-(3-methoxyphenoxy)propionitrile is described.

VON BRAUN (and, in part, O. Bayer), having failed to effect the condensation of chroman-4-one with isatin under the alkaline conditions normally used to bring about the Pfitzinger reaction,

and finding that they could recover the isatin but not the chromanone, attempted to elucidate the action of alkali on chromanone (*Annalen*, 1927, **451**, 54). They showed that on warming with aqueous alcoholic alkali a brown solution was rapidly formed, but they failed to isolate any pure substance from the material which acid precipitated from this solution. They showed that the crude product had a molecular weight between 500 and 600.

We found that the products of alkali-catalysed condensations of chromanone with aromatic aldehydes are often very difficult to purify, compared with the same substances prepared in alcoholic hydrogen chloride or acetic acid–hydrogen chloride solutions. It appeared that this was caused by self-condensations of chromanones in alkaline media. Self-condensations of ketones are, of course, well known. Chromanone might, however, be expected to be rather

(I.) 



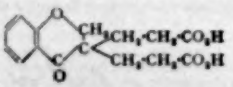
(II.)

more unreactive in this respect than a ketone like indan-1-one because of the neutralising effect of the oxygen atom (I), and accordingly we found no evidence of the formation of compounds analogous to anhydroindanone and truxene : chromanone was recovered unchanged after many hours' boiling with aqueous sulphuric acid or with alcoholic hydrogen chloride.

We suspected, therefore, from analogy with the conversion of flavanones into *o*-hydroxychalkones by alkali and the condensation of chalkone with flavanones in the presence of alkali (Kaplash, Shah, and Wheeler, *J. Indian Chem. Soc.*, 1942, **19**, 117), that the changes that chromanone undergoes in alkaline media might depend on a preliminary ring opening with the formation of *o*-hydroxyphenyl vinyl ketone rather than on an aldol-type reaction. It appears likely that this is so.

We, too, failed to obtain any crystalline material from the product obtained by warming chromanone with aqueous sodium hydroxide, but from the material formed when chromanone is boiled with alcoholic sodium ethoxide, three crystalline compounds have been isolated. All appear to be polymers of the parent substance. Two were obtained only in very small yield. Of these, (*A*), m. p. 107°, is a colourless neutral substance $(C_9H_8O_2)_x$, and (*B*), m. p. 172°, is a colourless alkali-soluble (phenolic) compound $(C_9H_8O_2)_x$. (*A*) is converted into (*B*) by the action of sodium hydroxide. They have not, so far, been further investigated.

The third product of the reaction, m. p. 142°, is most probably 3 : 3-di-(2-*o*-hydroxybenzoylethyl)chroman-4-one (II; R = OH), formed by interaction of chromanone and two molecules of *o*-hydroxyphenyl vinyl ketone. This constitution has not been proved, but there appears sufficient evidence to justify the formula (II; R = OH) for the compound, m. p. 142°. The substance is insoluble in aqueous sodium carbonate, but it dissolves slowly in dilute sodium hydroxide, forming a pale yellow solution from which it is reprecipitated by acid. Addition of benzenediazonium chloride to the alkaline solution gives an orange-coloured precipitate, and when an alcoholic solution of (II; R = OH) is treated with aqueous ferric chloride a brownish-violet coloration is produced. Acetylation gives a diacetyl derivative (II; R = OAc) which can be hydrolysed to give (II; R = OH) again. Methylation with methyl iodide and potassium carbonate affords a dimethoxy-compound (II; R = OMe) which is no longer soluble in alkali, suggesting that phenolic hydroxyl groups have been methylated. The molecular weight of 3 : 3-di-(2-*o*-hydroxybenzoylethyl)chroman-4-one, determined by Rast's method, was discordant, but the molecular weight of the diacetyl derivative (II; R = OAc), determined cryoscopically in benzene, was correct. The compound (II; R = OH) forms a dioxime and a bisphenylhydrazone as would be expected, because it is unlikely that the carbonyl group in the ring would



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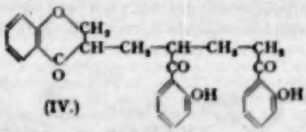


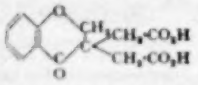
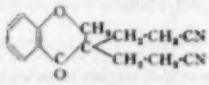
(IV.)

react easily with ketonic reagents. [It has been shown that 3 : 3-di-(2-carboxyethyl)chroman-4-one (III) does not react with hydroxylamine even on long boiling : the crude recovered substance does not contain nitrogen.] The compound (II; R = OH) took up about two molecules of

bromine in acetic acid solution, and on hydrogenation in the presence of Adams's catalyst, about four molecules of hydrogen were slowly absorbed to give a product that was essentially non-phenolic. Neither of these reactions, however, afforded crystalline material.

These facts do not exclude the formula (IV) for the substance, m. p. 142°, though this might perhaps be expected to yield a trioxime; the structure (II; R = OH) is, however, preferred for another reason given later.

An attempt was made to oxidise the dimethoxy-compound (II; R = OMe) with selenium dioxide in the hope that if formula (II; R = OH) is correct a tetraketone would be formed and could be degraded to give (V) (compare Morrell, Pickering, and Smith, *J. Inst. Petroleum*, 1948, **34**, 667). The dimethoxy-compound, however, failed to react at all with selenium dioxide: it appears that the carbonyl groups in this substance are comparatively unreactive as it also fails to form an oxime. Oxidation of the diacetyl compound (II; R = OAc) with selenium dioxide took place, but the yellow product of the reaction failed to give (V) on further oxidation with

(V.)   (VI.)

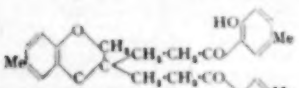
hydrogen peroxide and sodium hydroxide. The only crystalline product isolated from the alkaline solution so obtained was salicylic acid, although a small quantity of a phenolic substance, m. p. 119—120°, and not identified, was obtained from the solid residue. The results of the experiment were therefore inconclusive.

It has been shown that phenyl vinyl ketone reacts with chromanone in the presence of sodium ethoxide to give a small yield of 3 : 3-di-(2-benzoylethyl)chroman-4-one (II; R = H); this substance was also obtained when phenyl vinyl ketone was prepared from 2-chloropropiophenone in the presence of chromanone (compare Allen and Bridgess, *J. Amer. Chem. Soc.*, 1929, **51**, 2151). In both reactions most of the phenyl vinyl ketone polymerised to a gum. (II; R = H) has also been synthesised. Acrylonitrile condensed smoothly with chromanone in dioxan solution to give 3 : 3-di-(2-cyanoethyl)chroman-4-one (VI). The acid chloride corresponding to (VI) reacted with benzene in the presence of aluminium chloride to give 3 : 3-di-(2-benzoylethyl)-chroman-4-one, identical with the substance prepared as described above.

The formation of (II; R = H) from chromanone and phenyl vinyl ketone supports the formula (II; R = OH) for the compound, m. p. 142°, because by analogy with the reactions of acrylonitrile with other ketones, there can be no doubt that the dicyanide formed here is 3 : 3-di-(2-cyanoethyl)chroman-4-one (VI).

An unsuccessful attempt to synthesise (II; R = OH) was made by heating the diphenyl ester of (III) with aluminium chloride under conditions favourable to bringing about an ortho-Fries rearrangement. The product, m. p. 185—200°, although it could not be obtained in a chemically pure condition, seemed to be essentially $C_{17}H_{16}O_4$, but it appears probable, in view of the higher m. p., that at any rate part of the change has involved a *para*-rearrangement. The failure of this reaction to produce the substance considered to be (II; R = OH) in no way disproves the proposed formula. Attempts have also been made to prepare (II; R = OMe) by decomposing various Mannich bases from *o*-methoxyacetophenone in the presence of chromanone, but so far this method has not led to success. The hydrochloride of *o*-hydroxyphenyl 2-dimethylaminoethyl ketone has been prepared, but when it was decomposed by boiling with water in the presence of chromanone an uncrystallisable gum and not (II; R = OH) was obtained. A similar gummy product, and not chromanone, resulted when it was refluxed with water.

Direct synthesis of (II; R = OH) by a Friedel–Crafts reaction similar to that used to prepare (II; R = H) is impossible because this would require *o*-substitution into the phenol or anisole nucleus, and so far attempts to synthesise (VII), which might be expected to be formed from 6-methylchromanone, have not been pursued very far because the product actually obtained from 6-methylchromanone is very difficult to purify.



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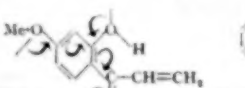

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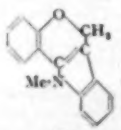

(IX.)

It is clear that substituents in the chromanone nucleus modify the ease of polymerisation very greatly. For instance, 7-methoxychromanone has been recovered almost quantitatively after 2 hours' boiling with alcoholic sodium ethoxide, although much longer boiling gradually converts it into a phenolic substance which is being investigated. The methoxyl group clearly makes the chromanone ring harder to open and, indeed, 2-hydroxy-4-methoxyphenyl vinyl ketone (VIII), which it should give if ring opening occurred, has been prepared and found to be a stable yellow substance that shows no tendency to polymerise and is actually cyclised to give 7-methoxychromanone with aqueous sodium hydroxide. Bergel, Haworth, Morrison, and Rinderknecht (*J.*, 1944, 163) claim to have prepared the dinitrophenylhydrazone from 2-hydroxy-4-methoxyphenyl vinyl ketone obtained by decomposing an appropriate Mannich base. The substance that they describe is almost certainly the isomeric 2 : 4-dinitrophenylhydrazone of 7-methoxychromanone. This substance has now been made and shown to melt at 245°, as does the compound described by these authors. The vinyl compound (VIII) yields, with dinitrophenylhydrazine, a product that has not been obtained in a crystalline condition, and (VIII) can be reconverted into 2-hydroxy-4-methoxyphenyl 2-chloroethyl ketone from which it was prepared, by treatment with hydrochloric acid.

Like Harradence, Hughes, and Lions (*J. Proc. Roy. Soc. N. S. Wales*, 1938, **72**, 273), we were unable to prepare an indole from chromanone phenylhydrazone and we also found that the *p*-nitrophenylhydrazone was unaffected by acid reagents. Chromanone phenylmethylhydrazone, however, yielded 1′-methylindolo(3′ : 2′-3 : 4)chrom-3-en (IX) on treatment with dilute sulphuric acid.

Experimental.

Chroman-4-one.—Chromanone was prepared by Powell's method (*J. Amer. Chem. Soc.*, 1923, **55**, 2711) which we found preferable to Arndt and Kallner's (*Ber.*, 1924, **57**, 204). The use of *dry* benzene did not increase the yield (52%) and we found purification by steam distillation best.

β-(3-Methoxyphenoxy)propionitrile (prepared from resorcinol monomethyl ether and acrylonitrile by the method since described by Bachmann and Levine, *J. Amer. Chem. Soc.*, 1948, **70**, 599, but with use of a little sodium as condensing agent) decomposes very readily on distillation (b.p. 191—195°/15 mm.) unless it is quite free from all traces of the alkali used to remove the unchanged phenol.

β-(3-Methoxyphenoxy)propionic Acid.—The above nitrile (5 g. on refluxing for 8 hours with concentrated hydrochloric acid (50 c.c.) affords β-(3-methoxyphenoxy)propionic acid, m. p. 82°, best purified by extraction in a Soxhlet apparatus with petroleum (b.p. 40—60°) (yield 4 g.). If decomposition products of the nitrile are present in the material subjected to hydrolysis, the acid obtained is very difficult to purify.

β-(4-Methylphenoxy)propionitrile, prepared as above from *p*-cresol and acrylonitrile, separates from methyl alcohol as colourless needles, m. p. 48° (Found : N, 8·3. $C_{10}H_{11}ON$ requires N, 8·7%).

7-Methoxychroman-4-one.—β-(3-Methoxyphenoxy)propionitrile (5 g.) and powdered anhydrous zinc chloride (5 g.) in dry ether (20 c.c.) were treated with dry hydrogen chloride at 0° for 4 hours, and the mixture was kept at room temperature until next day. The crystalline solid formed was separated, washed with ether, and refluxed with water for one hour, a yellow oil being obtained. This was extracted with ether and dried (Na_2SO_4), and the solvent removed. Distillation *in vacuo* (b. p. 197°/30 mm.) gave 7-methoxychromanone, identical (mixed m. p.) with that substance, m. p. 76—78°, prepared as described by Perkin, Ray, and Robinson (*J.*, 1926, 946) (yield, 3·5 g.). Bachmann and Levine (*loc. cit.*) found cyclisation of this nitrile with sulphuric acid or phosphoric oxide unsatisfactory. When 7-methoxychromanone (0·6 g.) and 2 : 4-dinitrophenylhydrazine (0·5 g.) were melted together on a steam-bath the product solidified and, after extraction with hot alcohol, a red solid, m. p. 244—245°, remained. Recrystallisation from glacial acetic acid afforded *7-methoxychromanone* 2 : 4-*dinitrophenylhydrazone* as red needles, m. p. 245° (Found : C, 53·8; H, 3·9. $C_{16}H_{14}O_5N_4$ requires C, 53·6; H, 3·9%).

Polymerisation of Chroman-4-one.—Chromanone (20 g.) was refluxed for 1½ hours with an alcoholic solution of sodium ethoxide [sodium (3·2 g.) in alcohol (170 c.c.)]; the mixture was then stirred into dilute hydrochloric acid, and the semi-solid mass which was precipitated crystallised when treated with ether. Recrystallisation from alcohol gave 3 : 3-*di*-(2-o-*hydroxybenzoylethyl*)*chroman-4-one* (II ; R = OH) as colourless needles, m. p. 142° (5·6 g.) (Found : C, 72·9; H, 5·4. $C_{27}H_{24}O_5$ requires C, 72·9; H, 5·4%). The aqueous acid from the above was extracted with ether which was then combined with that from which (II ; R = OH) first separated, and the ethereal solution so obtained was washed with sodium hydroxide (10%). After drying (Na_2SO_4) and distillation of the ether, a crystalline *solid* (*A*) remained. Recrystallisation from methyl alcohol afforded colourless plates, m. p. 107° [Found : C, 72·8; H, 5·0%; *M* (Rast), 276. $(C_9H_8O_3)_3$ requires C, 72·9; H, 5·4%; *M*, 296]. Acidification of the above aqueous sodium hydroxide and extraction with ether gave a little more of the compound, m. p. 142°, and a small quantity of a *substance* (*B*), ultimately obtained as colourless needles, m. p. 172°, from alcohol [Found : C, 72·4; H, 5·3. $(C_9H_8O_3)_n$ requires C, 72·9; H, 5·4%]. When (*A*), which is insoluble in cold alkali, was boiled for 5 minutes with sodium hydroxide (10%) a clear yellow solution was obtained and acidification afforded (*B*), m. p. 172°, after recrystallisation from alcohol.

Derivatives and Reactions of 3 : 3-*Di*-(2-o-*hydroxybenzoylethyl*)*chroman-4-one* (II ; R = OH).—This compound (2 g.), methyl iodide (10 c.c.), dry potassium carbonate (20 g.), and acetone (60 c.c.) were refluxed together for 6 hours. The solvent was distilled, water was added, and extraction of the residue

with ether gave, after drying (Na_2SO_4) and evaporation, a colourless gum which crystallised when treated with methyl alcohol. **3 : 3-*Di*-(2-o-*methoxybenzoylethyl*)*chroman*-4-*one*** was obtained as colourless prisms, m. p. 176°, from methyl alcohol (Found : C, 73·5; H, 6·0. $C_{26}H_{24}O_6$ requires C, 73·7; H, 5·9%). Methylation with methyl sulphate and sodium hydroxide was not successful. The compound (II; R = OH) (1·8 g.) in dry pyridine was treated with excess of acetic anhydride. After 12 hours, dilute hydrochloric acid was added and a gum separated. This crystallised with alcohol and was recrystallised from alcohol, **3 : 3-*di*-(2-o-*acetoxybenzoylethyl*)*chroman*-4-*one*** separating as colourless needles, m. p. 135—139° (1·05 g.) (Found : C, 70·2; H, 5·4%; *M* (cryoscopic in benzene), 535. $C_{31}H_{28}O_8$ requires C, 70·4; H, 5·3%; *M*, 528). Careful purification did not change the m. p. The same compound can be obtained if (II; R = OH) is boiled with acetic anhydride and a little fused sodium acetate for exactly 4 minutes; longer boiling produces an uncrystallisable gum. Hydrolysis was effected when the diacetyl compound (0·3 g.) was suspended in a little alcohol with sodium hydroxide (0·2 g.) and the mixture was kept overnight. Acidification of the yellow solution formed gave a solid which, after recrystallisation, melted at 142° alone or mixed with (II; R = OH). The compound (II; R = OH) (1 g.), hydroxylamine hydrochloride (2 g.), and crystalline sodium acetate (4 g.) were refluxed in alcohol for 4 hours. Dilution with water precipitated a white solid which was recrystallised from alcohol and then acetic acid. A ***dioxime*** was obtained as colourless needles, m. p. 213—221° (decomp.) (Found : C, 68·8; H, 5·6; N, 5·5. $C_{31}H_{30}O_6N_2$ requires C, 68·3; H, 5·5; N, 5·9%). The compound (II; R = OH) (0·5 g.) was warmed on a steam-bath with excess of phenylhydrazine for 5 minutes, and rubbing with acetic acid precipitated a solid which crystallised from alcohol. Recrystallisation from acetic acid yielded a ***bisphenylhydrazone*** as yellow plates, m. p. 230—233° (decomp.) (Found : C, 74·8; H, 6·2; N, 8·1. $C_{38}H_{34}O_4N_4$ requires C, 75·0; H, 5·6; N, 9·2%).

Oxidation of **3 : 3-*Di*-(2-o-*acetoxybenzoylethyl*)*chroman*-4-*one***.—A mixture of the diacetyl compound (3 g.), dioxan (25 c.c.), and selenium dioxide (1·4 g.) was refluxed for 3 hours; a further quantity of selenium dioxide (1·4 g.) was then added, and boiling continued for 6 hours more. The solution was decanted from the selenium into water, and the precipitate formed was dissolved in ether and dried ($MgSO_4$), the solvent removed, and the residue suspended in hydrogen peroxide (50 c.c.; 30%) and carefully treated with sodium hydroxide (7·5 g. in water, 40 c.c.) with constant mixing. After 2 hours the alkaline solution was separated from some solid, washed with ether, acidified, and extracted many times with ether. From this extract salicylic acid was the only crystalline material isolated. From the solid above, a very small quantity of an unidentified phenolic substance, colourless plates, m. p. 119—120°, from alcohol, was obtained (Found : C, 69·2; H, 5·0%).

3 : 3-*Di*-(2-*cyanoethyl*)*chroman*-4-*one*.—Chromanone (20 g.) in pure dioxan (60 c.c.) and methyl-alcoholic potassium hydroxide (2 c.c.; 30%) was treated with acrylonitrile (14·3 g.), dropped in with vigorous stirring during one hour. Stirring was continued at room temperature for 8 hours. After dilution with water and acidification with hydrochloric acid, the dioxan and other unchanged materials were steam-distilled. The resulting brown oil crystallised from alcohol and was recrystallised first from alcohol and then from acetic acid, **3 : 3-*di*-(2-*cyanoethyl*)*chroman*-4-*one*** separating as colourless prisms, m. p. 87° (Found : C, 71·3; H, 5·4. $C_{15}H_{14}O_2N_2$ requires C, 70·9; H, 5·5%).

3 : 3-*Di*-(2-*carboxyethyl*)*chroman*-4-*one*.—The above cyanide was hydrolysed by boiling it with concentrated hydrochloric acid. The product was purified by dissolving it in sodium carbonate, washing with ether, reprecipitating with acid, and recrystallising from aqueous acetic acid (50%), from which **3 : 3-*di*-(2-*carboxyethyl*)*chroman*-4-*one*** separated as colourless prisms, m. p. 169°, sintering at 155° (17 g.) (Found : C, 61·2; H, 5·6%; equiv., 144·8. $C_{15}H_{14}O_6(CO_2H)_2$ requires C, 61·6; H, 5·5%; equiv., 146·5). Crude **3 : 3-di-(2-chloroformylethyl)chroman-4-one** was prepared by boiling this acid with excess of thionyl chloride for 2 hours. After removal of thionyl chloride, the acid chloride remained as a syrup. It could be hydrolysed to the acid with water.

3 : 3-*Di*-(3-*benzoylethyl*)*chroman*-4-*one*.—(*a*) The above acid chloride (1·4 g.) was dissolved in pure benzene (20 c.c.) and treated with aluminium chloride (1·0 g.). After 1½ hours the mixture was refluxed for 20 minutes, acidified with hydrochloric acid, and the benzene removed in steam. The product was separated and crystallised in contact with ether. Recrystallisation from acetic acid afforded a small quantity of **3 : 3-di-(2-*benzoylethyl*)*chroman*-4-*one*** as colourless needles, m. p. 185—187°, identical (mixed m. p.) with the substance described below.

(*b*) Chromanone (4·5 g.), 2-chloropropiophenone (10·4 g.), and potassium acetate (10 g.) were mixed in methyl alcohol (60 c.c.), and during 1½ hours a solution of sodium (1·4 g.) in methyl alcohol (48 c.c.) was added as the solution boiled under reflux. Dilute acid was then added, methyl alcohol and chromanone were steam-distilled, and the residual solid crystallised from glacial acetic acid as colourless needles, m. p. 185—187° (Found : C, 78·3; H, 6·0. $C_{15}H_{14}O_4$ requires C, 78·6; H, 5·8%) (yield 0·3 g.).

(*c*) Freshly prepared phenyl vinyl ketone (7 g.) and chromanone (3·9 g.) were added to a solution of sodium (0·6 g.) in alcohol (25 c.c.), and after the mixture had boiled for one hour the solution was decanted from the resin formed, into dilute acid which was then extracted with ether. The ether was washed with sodium hydroxide, dried (Na_2SO_4), and distilled. A small quantity of **3 : 3-di-(2-benzoylethyl)chroman-one**, m. p. 185—187° (from alcohol), was obtained.

3 : 3-*Di*-(2-*dicarbophenoxyethyl*)*chroman*-4-*one*.—Crude **3 : 3-di-(2-chloroformylethyl)chroman-4-one** (17 g.) and phenol (10·2 g.) were heated together on a steam-bath for 2 hours. The product was dissolved in ether, and the solution washed with sodium hydroxide; much of the product crystallised from the ether and was filtered off. The ether was dried ($MgSO_4$) and evaporated. The total solid was recrystallised from alcohol, and **3 : 3-*di*-(2-*carbophenoxyethyl*)*chroman*-4-*one*** separated as colourless prisms, m. p. 102° (Found : C, 72·7; H, 5·3. $C_{31}H_{28}O_8$ requires C, 72·9; H, 5·4%) (10·5 g.). When this ester (6·5 g.) and aluminium chloride (13 g.) were heated together in an oil-bath at 160° for 1½ hours and the product was treated with dilute hydrochloric acid, a brown gum was obtained. This was dissolved in glacial acetic acid, filtered, and precipitated with water, and the solid so obtained was dissolved in ether and

dried (Na_2SO_4). On concentration, crystalline material separated, but repeated recrystallisation from acetic acid failed to produce completely homogeneous material; the m. p. was 185—200° (Found: C, 72·0; H, 5·3. Calc. for $C_{11}H_{14}O_4$: C, 72·9; H, 5·4%).

o-Hydroxyphenyl 2-Dimethylaminoethyl Ketone Hydrochloride.—A mixture of *o*-hydroxyacetophenone (7·5 g.), methylamine hydrochloride (6 g.), paraformaldehyde (2·25 g.), and alcohol (15 c.c., containing four drops of hydrochloric acid) was refluxed for one hour. On cooling, the salt crystallised and recrystallisation from alcohol gave *o-hydroxyphenyl 2-dimethylaminoethyl ketone hydrochloride* as colourless prisms, m. p. 176° (Found: N, 6·0. $C_{11}H_{16}O_2NCl$ requires N, 6·1%). This salt decomposed to give a yellow gum when boiled with water, or with chromanone and water.

2-Hydroxy-4-methoxyphenyl 2-Chloroethyl Ketone.—β-Chloropropionic acid (10 g.) and phosphorus trichloride (9 g.) were heated together on a steam-bath until the reaction was over, and then benzene (100 c.c.) was added. The mixture was decanted from the phosphorous acid, mixed with resorcinol dimethyl ether (14 g.), and slowly added to aluminium chloride (15 g.) cooled in ice, and after an hour at room temperature it was heated on a steam-bath for one hour. On pouring into ice–dilute hydrochloric acid some solid separated. This was filtered off and the benzene layer was dried (Na_2SO_4) and evaporated, giving a further quantity of solid. The two were combined and recrystallised from alcohol, *2-hydroxy-4-methoxyphenyl 2-chloroethyl ketone* separating as colourless prisms, m. p. 93—94° (7·5 g.) (Found: C, 55·9; H, 5·2. $C_{11}H_{13}O_3Cl$ requires C, 55·6; H, 5·1%).

2-Hydroxy-4-methoxyphenyl Vinyl Ketone.—The above chloro-compound (4 g.) and anhydrous potassium acetate (2 g.) were refluxed in alcoholic solution for ½ hour and poured into water. A yellow solid separated and was dried. Recrystallisation from petroleum (b. p. 40—60°) gave *2-hydroxy-4-methoxyphenyl vinyl ketone* as yellow prisms, m. p. 53°, in almost quantitative yield (Found: C, 67·5; H, 5·4. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). Treatment with warm concentrated hydrochloric acid reconverted it into 2-hydroxy-4-methoxyphenyl 2-chloroethyl ketone, and with dinitrophenylhydrazone, either in alcohol or without a solvent, it reacted to form a resinous mass which did not crystallise. It dissolved freely in aqueous sodium hydroxide (10%) to give a yellow solution, the colour of which faded during a few minutes as an oil separated and finally crystallised. It was 7-methoxychromanone, m. p. 78°, identical (mixed m. p.) with the substance described by Perkin, Ray, and Robinson (*loc. cit.*). This chromanone condensed with veratraldehyde, in the presence of alcoholic hydrogen chloride, to give 7-methoxyveratrylidene-chromanone, m. p. 141°, identical (mixed m. p.) with that substance obtained by the above authors (*loc. cit.*).

1'-Methylindolo(3' : 2'-3 : 4)*chromo-3-en.*—Chromanone (5 g.) and phenylmethylhydrazone (4·1 g.) were heated for ½ hour on a steam-bath, and on being dissolved in a little alcohol and set aside, the product slowly crystallised. Recrystallisation from alcohol gave *chromanone phenylmethylhydrazone* as yellow prisms, m. p. 70° (1·9 g.) (Found: C, 76·5; H, 6·5. $C_{16}H_{14}ON_2$ requires C, 76·2; H, 6·3%). This was suspended in dilute sulphuric acid (30 c.c. of 20% by vol.). It dissolved slowly, and the indole began to separate. After being warmed on a steam-bath for a few minutes, the mixture was set aside for 24 hours, during which the product solidified. Recrystallisation from aqueous alcohol afforded *1'-methylindolo*-(2' : 3' -3 : 4)*chromo-3-en* in two different forms, colourless needles, m. p. 115°, and colourless plates, m. p. 117° (mixed m. p. 116°) (Found: C, 81·6; H, 5·7. $C_{18}H_{13}ON$ requires C, 81·7; H, 5·5%) (yield 0·9 g.).

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466. *Synthetical Experiments in the Chelidonine–Sanguinarine Group of the Alkaloids. Part III.*

By A. S. BAILEY, SIR ROBERT ROBINSON, and R. S. STAUNTON.

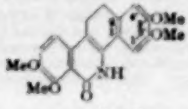
7 : 8 : 2' : 3'-Tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridone of which the synthesis was described in Part II (*J.*, 1950, 1375) has been converted into the related tetramethoxybenzphenanthridine. The methosulphate of the latter base is changed on reduction into a tetramethoxy-*N*-methyldihydrobenzphenanthridine which has been obtained by Späth and Kuffner (*Ber.*, 1931, **64**, 3034) from either sanguinarine or chelerythrine. The synthesis of the reference compound confirms the correctness of the structures of these two alkaloids deduced from degradative evidence.

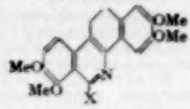
The work of Part I in an isomeric series has been carried further and the tetramethoxy-*N*-methylbenzphenanthridinium salt which is an analogue of sanguinarine has been prepared.

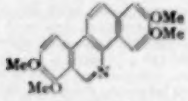
7 : 8 : 2' : 3'-TETRAMETHOXY-3 : 4-DIHYDRO-1 : 2-BENZPHENANTHRIDONE * (I) is changed by phosphoryl chloride into 9-chloro-7 : 8 : 2' : 3'-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (II; X = Cl) which easily affords a 9-anilino-derivative (II; X = NHPh). The chloro-compound is reduced by hydrogen in the presence of palladised strontium carbonate to 7 : 8 : 2' : 3'-tetramethoxy-3 : 4-dihydrobenzphenanthridine (II; X = H), which is dehydrogenated by means of palladised charcoal in boiling *p*-cymene solution with formation

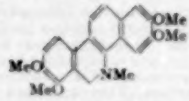
* A misprint occurs in the numbering of this formula in *J.*, 1950, 1377, where it is allotted number (VIII).

of 7 : 8 : 2′ : 3′-tetramethoxybenzphenanthridine (III). It is also possible to transform (II; X = Cl) into (III) in one operation under similar conditions.









The methosulphate of (III) could be reduced by means of zinc and aqueous hydrochloric acid to 7 : 8 : 2′ : 3′-tetramethoxy-10-methyl-9 : 10-dihydro-1 : 2-benzphenanthridine (IV), which was identical with a specimen prepared by S. N. Sarkar from dihydrosanguinarine (replacement of two methylenedioxy- by four methoxy-groups) using the method of Späth and Kuffner (*Ber.*, 1931, **64**, 3034). We are grateful to Dr. Sarkar for the provision of this valuable specimen. The identity was established by mixed melting points. Further, we are deeply indebted to Mrs. D. M. Hodgkin and Miss P. M. Cowan (Department of Crystallography, Oxford University) for their examination of the crystals of the two specimens: they were reported to be identical.

Fig. 1.

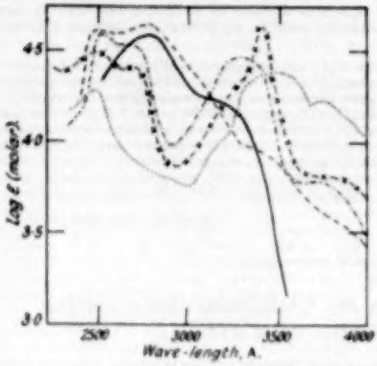


Fig. 2.

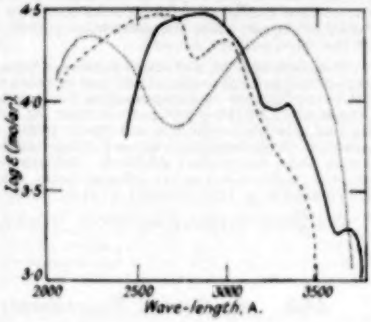


Fig. 1. ..... 7 : 8 : 2′ : 3′-*Tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridone* (*in* $CHCl_3$).
– – – – – – – – 7 : 8 : 2′ : 3′-*Tetramethoxy*-1 : 2-*benzphenanthridine* (*in* $CHCl_3$).
——— 7 : 8 : 2′ : 3′-*Tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine* (*in* EtOH).
× — × — × 9-*Chloro*-7 : 8 : 2′ : 3′-*tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridine* (*in* EtOH).
—·—·—·— 7 : 8 : 2′ : 3′-*Tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridine* (*in* EtOH).

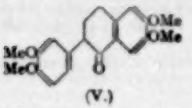
Fig. 2. ——— 6 : 7 : 2′ : 3′-*Tetramethoxy*-1 : 2-*benzphenanthridine* (*in* $CHCl_3$).
– – – – – – – – 6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)*naphthalene* (*in* EtOH).
..... 6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-3 : 4-*dihydronaphthalene* (*in* EtOH).

Since Sarkar (*Nature*, 1948, **162**, 265) found that sanguinarine chloride was toxic to rats it was of interest to examine the methochloride of (III) which is of sanguinarine type. This was kindly undertaken by Dr. L. A. Stocken (Biochemistry Department, Oxford University) who reports that the substance is not toxic to rats at the concentrations used in the case of sanguinarine.

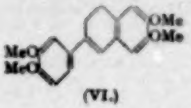
The synthesis of (V) was described in Part I (Richardson, Robinson, and Seijo, *J.*, 1937, 835) and this tetralone was converted into 6 : 7 : 2′ : 3′-tetramethoxy-3 : 4 : 11 : 12-tetrahydro-1 : 2-benzphenanthridine (tetrahydro-derivative of VII). The latter has now been

dehydrogenated to (VII); the metho-salts of this base are so sparingly soluble that their pharmacological properties could not be observed.

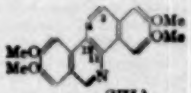
In applying the Leuchart reaction to (V) (main product, >CO ⟶ >CH·NH·CHO), a by-product, namely 6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-3 : 4-dihydronaphthalene (VI), was obtained. Two hydrogen atoms could be added to, or removed from, this substance with formation of the related tetralin or naphthalene derivative, respectively.



(V.)



(VI.)



(VII.)

The ultra-violet absorption of some of the new compounds is shown in Figs. 1 and 2. We are indebted to Dr. F. B. Strauss for these determinations. Comparison with the previously observed absorption of dihydrosanguinarine shows that the substitution of two methoxy-groups for a methylenedioxy-group has a considerable effect in this series. The ultra-violet absorption spectrum of (VI) is similar to that of *trans*-stilbene, and its dehydrogenation product (– – – – in Fig. 2) resembles the curve for 2-phenylnaphthalene in this respect (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 944; Bills and Noller, *ibid.*, 1948, **70**, 957; cf. Braude, *Ann. Reports*, 1945, **42**, 105).

Experimental.

9-Chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (II; X = Cl).—A mixture of 7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridone (6 g.) and phosphoryl chloride (30 c.c.) was refluxed (oil-bath at 140°) for 1 hour. Addition of the deep-red solution to ice, followed by treatment with ammonia gave a grey solid which was collected, washed well with water, dried, and extracted with boiling benzene (3 × 30 c.c.). The extracts were concentrated to approx. 30 c.c. and cooled, giving 5·6 g. of crude crystals. The *9-chloro*-compound crystallised from benzene in cream-coloured plates, m. p. 176—178°, which became slightly yellow when kept (Found: C, 65·2, 65·3; H, 4·9, 5·2; Cl, 9·9, 8·7. $C_{21}H_{20}O_4NCl$ requires C, 65·3; H, 5·2; Cl, 9·2%). It was insoluble in dilute mineral acids but dissolved in 6*N*-hydrochloric acid to a dark red solution from which an unstable hydrochloride separated. This lost hydrogen chloride at 70° giving the free base and the analysis was unsatisfactory.

9-Anilino-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine.—A solution of 9-chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (0·1 g.) in aniline (0·2 c.c.) was heated on a steam-bath. After 5 minutes needles started to separate from the mixture, and after 10 minutes the mixture was solid. Methanol (2 c.c.) was added, and the solid (m. p. 141—143°) collected, and crystallised from ethanol. The *9-anilino*-compound separated from ethanol as clusters of rods, m. p. 143—144° (Found: C, 73·1; H, 5·8; N, 6·2. $C_{27}H_{26}O_4N_2$ requires C, 73·3; H, 5·9; N, 6·3%). Solutions of the substance in organic solvents were colourless and exhibited an intense blue fluorescence; the yellow solutions in dilute mineral acids were non-fluorescent.

7 : 8 : 2′ : 3′-Tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (II; X = H).—A mixture of 9-chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (0·5 g.), potassium hydroxide (0·2 g.), 2-methoxyethanol (30 c.c.), and palladised strontium carbonate (0·5 g.) was shaken under hydrogen for 2 hours. The filtered solution was concentrated to a small volume and water added. The solid which separated (m. p. 161—162°; quantitative yield) was collected, washed with water, and crystallised from ethanol. *7 : 8 : 2′ : 3′-Tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine* formed colourless rods, m. p. 162—163° (Found: C, 71·5; H, 6·0; N, 4·1. $C_{21}H_{21}O_4N$ requires C, 71·9; H, 6·0; N, 4·0%). Solutions of the base in dilute mineral acids were yellow.

7 : 8 : 2′ : 3′-Tetramethoxy-1 : 2-benzphenanthridine (III).—(*a*) A solution of 9-chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (5 g.) in *p*-cymene (45 c.c.) was refluxed for 6 hours with palladised charcoal (0·6 g. of 30%) in a stream of hydrogen; evolution of hydrogen chloride had then almost ceased. The filtered solution slowly deposited a solid which, when collected and washed with light petroleum (b. p. 40—60°), had m. p. 210—214° (3·8 g.). This product was completely soluble in 2*N*-hydrochloric acid to a pale yellow solution and hence contained no trace of unchanged starting material. Crystallisation from pyridine–ethanol (4 : 1) gave a cream-coloured solid. A solution of the latter in chloroform–benzene (1 : 2 by vol.) was passed through an alumina column and the blue-violet fluorescent band (ultra-violet lamp) was eluted with the same mixture. Evaporation of the eluate and crystallisation of the residue from pyridine–ethanol gave *7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine* as colourless, lanceolate plates, m. p. 218—219° (decomp.) (Found: C, 71·8, 72·1; H, 5·4, 5·3; N, 3·9. $C_{21}H_{19}O_4N$ requires C, 72·3; H, 5·5; N, 4·0%). Solutions of the compound showed a weak blue-violet fluorescence in daylight; they were intensely fluorescent in ultra-violet light.

(*b*) A solution of 7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (0·4 g.) in *p*-cymene (5 c.c.) was refluxed for 2 hours with palladised charcoal (0·1 g. of 30%), under hydrogen. The crude product, m. p. 205—210°, crystallised from pyridine–ethanol (4 : 1) in lanceolate plates (0·2 g.), m. p. and mixed m. p. with a specimen prepared as under (*a*) 217—219° (decomp.) (Found: C, 72·3; H, 5·6%).

The ***hydrochloride*** crystallised from ethanol–water (4 : 1) as clusters of tiny, golden-yellow needles, m. p. 265—267° (decomp.), freely soluble in water (Found: C, 59·5; H, 5·9. $C_{21}H_{19}O_4N,HCl,2H_2O$ requires C, 59·7; H, 5·7%).

Methosulphate. After a solution of 7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine (2 g.) had been boiled in purified xylene (80 c.c.) for a minute, methyl sulphate (5 c.c.) was added and the mixture refluxed for 40 minutes; a further 2 c.c. of methyl sulphate were added after 15 minutes. The orange-yellow solid which rapidly separated from the solution was collected next day and washed with light petroleum (b. p. 40—60°). The product (2·1 g.), m. p. 255—258° (decomp.), was easily soluble in water. Crystallisation from ethanol–water (8 : 1) gave the ***methosulphate*** as clusters of orange-yellow needles, m. p. 255—257° (decomp.) (Found: C, 56·5, 56·3; H, 5·5, 5·6; N, 2·3; S, 6·3. $C_{23}H_{23}O_4NS,H_2O$ requires C, 56·0; H, 5·5; N, 2·8; S, 6·5%).

Treatment of a solution of the salt in 50% aqueous ethanol with ammonium chloride solution gave long, silky needles of the corresponding ***chloride***, m. p. 207—210° (decomp.) (Found: C, 60·3; H, 6·2; Cl, 7·6. $C_{23}H_{23}O_4NCl,2H_2O$ requires C, 60·6; H, 6·0; Cl, 8·2%).

Addition of potassium cyanide to an aqueous solution of 7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine methosulphate containing a few drops of dilute hydrochloric acid gave a white precipitate of *9-cyano*-7 : 8 : 2′ : 3′-*tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine*, which crystallised from ethyl acetate in colourless rhombs, m. p. 178—180° (decomp.) (Found: C, 70·6; H, 5·6; N, 6·8. $C_{24}H_{24}O_4N_2$ requires C, 70·8; H, 5·6; N, 7·2%).

7 : 8 : 2′ : 3′-*Tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine* (IV).—A mixture of 7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine methosulphate (1 g.), water (150 c.c.), concentrated hydrochloric acid (10 c.c.), and granulated zinc (20 g.) was refluxed, concentrated hydrochloric acid (10 c.c.) being added at hourly intervals. After 3 hours the solution had a very pale yellow colour, and a cream-coloured solid began to separate. The liquid was decanted and kept in the refrigerator overnight, and the solid was then collected, washed with water, and shaken with chloroform and 5*N*-ammonia. The chloroform extract was washed with water and dried ($MgSO_4$), the solvent removed, and the semi-solid residue digested with methanol (10 c.c.). Crystallisation of the resulting solid from chloroform–methanol gave a grey solid, m. p. 180—183° (0·31 g.). Sublimation at 170°/10^{-4} mm. gave a product, m. p. 182—184°. A benzene solution of the latter was chromatographed on alumina, forming a blue-fluorescent band (ultra-violet lamp). This was eluted with benzene, the eluate evaporated, and the residue crystallised from ethanol. 7 : 8 : 2′ : 3′-*Tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine* formed colourless prisms, m. p. 183·5—185° (slight decomp.) (Found: C, 72·6, 72·7, 72·4; H, 6·5, 6·1, 6·4; N, 3·9. Calc. for $C_{24}H_{25}O_4N$: C, 72·3; H, 6·3; N, 3·5%). The m. p. was not depressed by a specimen of the substance supplied by Dr. S. N. Sarkar; the ultra-violet absorption spectra of both specimens were identical.

Mrs. D. M. Hodgkin and Miss P. M. Cowan report that both specimens crystallise in the form of strongly birefringent plates, elongated along *b*. The crystals are biaxial positive with slow extinction parallel to the longest edge *b*. Powder and "single" crystal photographs show that the two specimens are identical, the unit cell is monoclinic, and the space group $P_{2_1/a}$. Cell dimensions are: $a = 21·36$; $b = 13·39$; $c = 13·73$ A.; $\beta = 108°$.

The substance is insoluble in dilute mineral acid. Suspensions in aqueous acids become yellow on the addition of a drop of ferric chloride solution, owing to oxidation to the quaternary salt.

β-(3 : 4-*Dimethoxybenzoyl*)-α-(3 : 4-*dimethoxyphenyl*)*propionitrile*.—The following method is more convenient than that of Richardson, Robinson, and Seijo (*loc. cit.*). Potassium cyanide (22 g.) in water (40 c.c.) was added during 3 minutes to a stirred solution of veratrylideneacetoveratrone (50 g.) in 2-methoxyethanol (150 c.c.) containing glacial acetic acid (9 c.c.) at 100°. Heating was continued for a further 10 minutes (after 8 minutes a white solid began to separate). Water (75 c.c.) was then added and the mixture allowed to cool. The solid which separated was collected, washed well with water, and dried (46 g.); it had m. p. 141—143°. A specimen, crystallised from acetone, had m. p. and mixed m. p. 143—144°.

This nitrile was converted into 1-keto-6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene (V) as described in Part I (*loc. cit.*). The 2 : 4-*dinitrophenylhydrazone* formed crimson prisms (from dioxan), m. p. 228—229° (decomp.) (Found: C, 59·5; H, 5·0; N, 10·6. $C_{33}H_{32}O_8N_4$ requires C, 59·6; H, 5·2; N, 10·7%).

1-*Formamido*-6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* (cf. "Organic Reactions," Vol. V, p. 301).—A solution of the above tetralone (8 g.) in formamide (20 c.c.) containing formic acid (1 c.c.) and ammonium sulphate (1 g.) was refluxed for 3 hours (oil-bath; 180°), formic acid (1 c.c.) being added every hour. The cold mixture was diluted with water and then extracted with chloroform. The chloroform extract was washed with water and dried (Na_2SO_4), the solvent removed, and the residual oil triturated with methanol (8 c.c.). Next day the solid which had separated was collected and dried. This solid was digested with acetone (10 c.c.), and the acetone-insoluble fraction crystallised from dioxan–ethanol (9 : 1) (5·2 g. of m. p. 200—202°) (Found: C, 67·7; H, 6·7; N, 3·9. Calc. for $C_{21}H_{23}O_5N$: C, 67·5; H, 6·7; N, 3·9%). Richardson, Robinon, and Seijo (*loc. cit.*) give m. p. 202—203°.

The acetone extract was evaporated and the residue (m. p. 126—128°) crystallised from ethanol afforded hexagonal plates (*ca.* 1 g.) of 6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-3 : 4-*dihydronaphthalene* (VI), m. p. 129—130° [Found: C, 73·5; H, 6·9; *M* (cryoscopic in camphor), 321. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%; *M*, 326]. The substance decolorised alkaline permanganate solution.

Increasing the time of heating in the Leuchart reaction to 7 hours gave a 40% yield of the dihydronaphthalene.

6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—A solution of 6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-3 : 4-dihydronaphthalene (1·5 g.) in dioxan (10 c.c.) was hydrogenated at the room temperature over platinum oxide (50 mg.) as catalyst. After 1 mole of hydrogen had been absorbed the catalyst was removed, the solvent evaporated *in vacuo* on the steam-bath, and the residual oil triturated with light petroleum (b. p. 40—60°), giving a white solid, m. p. 104—110°. Two crystallisations from methanol gave **6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*** as colourless rhombs, m. p. 117—118° (Found : C, 73·0; H, 7·3. $C_{20}H_{24}O_4$ requires C, 73·2; H, 7·3%).

6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)*naphthalene*.—A mixture of 6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-3 : 4-dihydronaphthalene (0·5 g.) and palladised charcoal (0·1 g. of 30%) was heated at 240° (metal-bath) for 30 minutes. Hydrogen was rapidly evolved and the melt solidified on cooling. The solid was taken up in chloroform, the solvent removed, and ethanol added to the resulting syrup, which then solidified. Crystallisation from ethanol–dioxan (9 : 1) and then from benzene afforded **6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)*naphthalene*** (270 mg.) as very thin, irregular plates, m. p. 179—180° (Found : C, 74·3; H, 6·3. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

Equimolecular quantities of the naphthalene derivative and trinitrobenzene in hot ethanol gave an orange-coloured solution. Nevertheless, colourless plates of tetramethoxyphenylnaphthalene separated on cooling.

6 : 7 : 2′ : 3′-*Tetramethoxy*-1 : 2-*benzphenanthridine* (VII).—1-Formamido-6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene was converted into 6 : 7 : 2′ : 3′-tetramethoxy-3 : 4 : 11 : 12-tetrahydro-1 : 2-benzphenanthridine as described by Richardson, Robinson, and Seijo (*loc. cit.*). The substance formed colourless prisms from pyridine–ethanol, m. p. 230—231° (Found : N, 4·1. Calc. for $C_{21}H_{23}O_4N$: N, 4·0%).

(*a*) An attempt to dehydrogenate tetramethoxytetrahydrobenzphenanthridine in boiling *p*-cymene was unsuccessful because the product was almost insoluble therein and crystallised on the catalyst from which it was obtained in small quantity by chloroform extraction.

(*b*) The tetrahydro-compound (300 mg.) was heated at 240° (metal-bath) with palladised charcoal (100 mg. of 30%). It melted and resolidified almost immediately. After 40 minutes the temperature of the bath was raised to 310°, whereupon the solid again melted; after 10 minutes at this temperature the solid was sublimed at 260/0·1 mm. and the sublimate crystallised from pyridine, giving a product (130 mg.), m. p. 299—301°.

(*c*) The tetrahydro-compound (1 g.) was heated at 250° for 30 minutes with palladised charcoal (0·2 g. of 30%). The cold solid was powdered and extracted with chloroform (3 × 30 c.c.), the solvent removed, and the residue crystallised from pyridine (30 c.c.), giving **6 : 7 : 2′ : 3′-*tetramethoxy*-1 : 2-*benzphenanthridine*** (0·62 g.) as colourless, diamond-shaped plates, m. p. and mixed m. p. with the specimen prepared as under (*b*) 302—304° (decomp.) (Found : C, 72·4, 72·3; H, 5·4, 5·5; N, 4·2. $C_{21}H_{19}O_4N$ requires C, 72·3; H, 5·5; N, 4·0%). The base is insoluble in the common organic solvents except pyridine and nitrobenzene. The hydrochloride and sulphate are yellow solids which are extremely sparingly soluble in water, the liquid remaining colourless even on boiling.

Methosulphate. A solution of 6 : 7 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine (0·5 g.) in xylene (5 c.c.) and nitrobenzene (10 c.c.) was boiled for a short time and methyl sulphate (1 c.c.) then added to the boiling solution. A yellow precipitate rapidly formed and after 5 minutes the solution was cooled and ether (10 c.c.) added. The solid was collected and washed with ether (quantitative yield). Crystallisation from ethanol–water (1 : 1) gave **6 : 7 : 2′ : 3′-*tetramethoxy*-1 : 2-*benzphenanthridine methosulphate*** as fine, pale yellow needles, m. p. 305—308° (decomp.) (Found : C, 56·1; H, 5·4; N, 3·1. $C_{22}H_{23}O_8NS,H_2O$ requires C, 56·0; H, 5·5; N, 2·8%). The ***methochloride*** formed lemon-yellow needles (from water), m. p. 293—295° (decomp.) (Found : C, 63·0; H, 5·8. $C_{22}H_{23}O_4NCl,H_2O$ requires C, 63·2; H, 5·7%).

Addition of potassium cyanide to an aqueous solution of the methosulphate gave an amorphous white precipitate of the ***pseudocyanide***. This was extracted with chloroform, the solution washed with water and dried ($MgSO_4$), and the solvent removed. The resulting syrup solidified on the addition of methanol, and crystallisation of the crude product, m. p. 225°, from 2-methoxyethanol gave colourless prisms, m. p. 227—229° (decomp.) (Found : C, 70·5; H, 5·6; N, 7·1. $C_{22}H_{23}O_4N_3$ requires C, 70·8; H, 5·6; N, 7·2%).

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467. *Germanous Oxide and Sulphide.*

By David A. Everest and Henry Terrey.

Germanous hydroxide can be prepared in either a white or a coloured form, the difference being due to varying degrees of hydration and particle size. The acidic nature of germanous hydroxide has been investigated, but no support for the view (put forward by Hantzsch) that germanous hydroxide acts as germanoformic acid can be found. Similarly, with germanous sulphide, no acidic properties can be detected.

Germanous hydroxide was first investigated by Winkler (*J. pr. Chem.*, 1886, **34**, 177) and its preparation has been more recently described by Bardet and Tchakarian (*Compt. rend.*, 1928, **186**, 637) and by Dennis and Hulse (*J. Amer. Chem. Soc.*, 1930, **52**, 3553). The latter authors observed the ease with which germanous hydroxide was oxidised by air; they also showed that when the hydroxide was heated in a vacuum, water was continuously removed, no evidence of the formation of definite hydrates being obtained. Microscopic examination showed that the darkening in colour observed on dehydration was due to an increase in particle size.

Winkler's method of preparation consisted in the action of water on germanochloroform, a reaction also studied by Dennis and his co-workers (*J. Physical Chem.*, 1926, **30**, 1049). These authors observed that if germano-chloroform was first treated with a little water a white solid was formed, which, on standing in presence of excess water, changed to the characteristic red germanous hydroxide.

The method of preparation used in this research is that described by Dennis and Hulse (*loc. cit.*): a solution of germanium dioxide (0·25—0·5M.) in 6N-hydrochloric acid was reduced with excess of 30% hypophosphorous acid, and germanous hydroxide was then precipitated with an excess of dilute ammonia. Germanous hydroxide is very readily oxidised by air, and the precipitation and washing of the precipitate were carried out in an atmosphere of nitrogen. Thus prepared, germanous hydroxide is a yellow to red gelatinous substance, soluble in dilute hydrochloric acid. If the precipitation is carried out from a boiling solution, the product is dark brown and somewhat granular and dissolves much more slowly than does the yellow form in dilute hydrochloric acid.

If a concentrated solution (1·5—2·0M.) of germanium dioxide was reduced with excess of hypophosphorous acid, and the solution simply diluted with water, a thick white precipitate of germanous hydroxide was formed. In contact with the solution this white form of germanous hydroxide slowly darkened until the normal red modification was obtained. This change in colour was found to take place immediately on addition of alkali. The ease of solubility of the white modification in dilute hydrochloric acid was much greater than that of the coloured forms, the rate of solution falling off on going from the white to the brown modification. This white form of germanous hydroxide appears to be the white compound observed by Dennis and his co-workers (*loc. cit.*) on treating germano-chloroform with a little water.

It was not possible to analyse any of the samples of germanous hydroxide, attempts to dry them simply resulting in a continuous loss of water till germanous oxide was formed.

Germanous hydroxide in the above reactions resembles stannous hydroxide (Bury and Partington, *J.*, 1922, **121**, 1998; Straumanis and Strenk, *Z. anorg. Chem.*, 1933, **213**, 301). Stannous hydroxide when precipitated is white, but when it is warmed with a little sodium hydroxide or sodium carbonate solution, its colour darkens through yellow to reddish-brown and finally to the bluish-black of stannous oxide.

The Acidic Properties of Germanous Hydroxide.—From the position of germanium in the Periodic Table it would be expected that germanous hydroxide should show acidic properties, especially as the acidic nature of stannous hydroxide seems to have been definitely established (Schoider, *Angew. Chem.*, 1936, **49**, 255). The chief evidence for the alleged acidic nature of germanous hydroxide rests on experiments by Hantzsch (*Z. anorg. Chem.*, 1902, **30**, 316). He observed that there was a reduction in the conductivity of sodium hydroxide solutions on addition of germanous hydroxide. On the basis of his measurements he postulated that germanous hydroxide acted as a monobasic acid, germanoformic acid, H·GeO·OH. Hantzsch prepared his germanous hydroxide by Winkler's method (*loc. cit.*), *i.e.*, by passing hydrogen chloride over heated elementary germanium. However, as was observed by Dennis and his co-workers (*loc. cit.*) and by Delwaulle and François (*Compt. rend.*, 1949, **228**, 1007), germanochloroform thus prepared contains up to 30% of germanium tetrachloride. Hydrolysis of such a mixture would give a product containing germanium dioxide, which has acidic properties (see Gulezian and Muller, *J. Amer. Chem. Soc.*, 1932, **54**, 3142, 3151). Hantzsch

also did not take into account any diminution in the conductivity of the sodium hydroxide solution which would have occurred if colloidal solution of the germanous hydroxide had taken place with the resultant removal of ions from solution by adsorption at the surface of the colloidal germanous hydroxide particles.

Other references to the acidic nature of germanous hydroxide have been made by Tchakarian (*Compt. rend.*, 1934, **199**, 886), Royan and Schwarz (*Z. anorg. Chem.*, 1933, **211**, 412), and Brine (M.Sc. Thesis, London Univ., 1937). Tchakarian observed that if either germanous oxide or hydroxide was heated with 50% sodium hydroxide solution, hydrogen and sodium germanate were formed. He assumed that in dilute alkali sodium germanoformate was formed, but that this decomposed when the concentration of alkali was increased. He put forward no evidence, however, for the actual formation of sodium germanoformate. Royen and Schwarz observed that if the hydride $(GeH_2)_x$ was treated with alkali a red opaque solution was obtained, which was said to contain sodium germanite Na_2GeO_2, but they did not report any actual investigation of this solution. Brine attempted to detect the formation of germanite polarographically by using saturated solutions of germanous hydroxide in 0·1N-alkali. He did not take any precautions to ensure the absence of any quadrivalent germanium, but the only waves he obtained were due to this, for he had already studied its polarographic behaviour in acid and alkaline media. Dennis and Hulse (*loc. cit.*) observed that germanous hydroxide when freshly precipitated gave with alkali reddish opaque solutions which they thought to be colloidal.

There are clearly considerable discrepancies in the literature as to the nature of solutions of germanous hydroxide in alkali. It was hoped that information could be obtained by means of potentiometric titrations of aqueous solutions of germanous hydroxide with alkali, but its low solubility in water precluded this: we found 0·044%, whereas Robinson (*Ann. Reports*, 1944, **41**, 111) quotes 0·18%. Even our lower figure should be accepted with reserve, as it is quite possible that a large part of the germanous hydroxide was present in the colloidal form.

Similarly, attempts to obtain evidence from the solubility of germanous oxide in alkali solutions of different concentrations were not successful. No relation between the results could be observed, and it was uncertain if the measured solubilites were not all due to quadrivalent germanium, germanous oxide being slowly oxidised by cold alkaline solutions (Tchakarian, *loc. cit.*). The solubilities observed were considerably smaller than those found for stannous oxide in alkali by Garrett and Heiks (*J. Amer. Chem. Soc.*, 1941, **63**, 562).

The method eventually used was a variation of Hantzsch's conductometric method. Preliminary experiments on sodium hydroxide–germanous hydroxide systems showed that oxidation caused large conductivity changes owing to the formation of the acidic germanium dioxide. It was therefore very important to ensure complete absence of any quadrivalent germanium during the course of the experiments (see p. 2284). It was found that there was no reaction between germanous hydroxide and sodium hydroxide, and no acidic properties of germanous hydroxide could be detected. There is also practically no tendency for the formation of colloidal solutions if all the quadrivalent germanium is absent. It was found, however, that if these solutions were exposed to the air, and some quadrivalent germanium was formed by oxidation, colloidal solutions were readily formed; this phenomenon is also shown by germanous sulphide.

This lack of acidic properties of germanous hydroxide is at first sight somewhat surprising. However, by comparison with the potentials of the bivalent–quadrivalent couples for lead and tin, it was seen that the germanite ion would have an extremely high reduction potential in alkaline media:

$$2OH^- + PbO \longrightarrow PbO_2 + H_2O + 2\varepsilon^- \qquad E = -0{\cdot}250 \text{ volt}$$
$$3OH^- + H_2O + H{\cdot}SnO_2^- \longrightarrow Sn(OH)_6 + 2\varepsilon^- \qquad E = 0{\cdot}96 \text{ volt}$$

Latimer ("Oxidation Potentials," p. 136) has given a rough estimate of the corresponding germanium couple:

$$2OH^- + H{\cdot}GeO_3^- \longrightarrow H{\cdot}GeO_4^- + H_2O + 2\varepsilon^- \qquad E \sim 1{\cdot}4 \text{ volts}$$

It seems probable indeed that the fact that bivalent germanium can exist at all in alkaline media is due to the insolubility of germanous hydroxide. If the germanite ion did exist in alkaline media it would spontaneously decompose into germanate, with deposition of germanium and/or liberation of hydrogen. This conclusion is supported by Tchakarian's observations on the oxidation of bivalent germanium in alkaline media (*loc. cit.*). It is a well-known fact also that alkaline solutions of stannous hydroxide tend to decompose on standing, giving stannate and metallic tin.

Acidic Nature of Germanous Sulphide.—Germanous sulphide has been prepared by a number of workers, and observations on its solubility in alkalis have been made. The crystalline form was prepared by Dennis and Joseph (*J. Physical Chem.*, 1927, **31**, 1716) by reduction of germanium disulphide with hydrogen, and also by Pugh (*J.*, 1930, 2371) by the action of hydrogen and hydrogen sulphide on germanium dioxide at 700°; prepared in this manner, it is a dark red to black crystalline solid. The pure substance was insoluble in alkali at room temperature, but if finely divided it was soluble in hot dilute caustic alkali.

Johnson and Wheatley (*Z. anorg. Chem.*, 1934, **216**, 273) also prepared crystalline germanous sulphide by direct volatilisation out of germanite. They found the crystalline material to be somewhat soluble in caustic alkali. They also prepared amorphous germanous sulphide, as did Dennis and Hulse (*loc. cit.*); this form was found to be readily soluble in dilute caustic alkalis. None of these authors claimed that these alkaline solutions contain thiogermanites and it seems to be implied, although it is not stated, that these solutions are actually colloidal. In view of the fact that germanites do not appear to exist, the nature of these solutions was reinvestigated, especially as none of the above authors recorded any precautions to exclude air when observing the solubility of germanous sulphide in alkali.

Amorphous germanous sulphide was used throughout this work. This substance is difficult to obtain in a state of purity, a small percentage of quadrivalent germanium usually being present. It was found that when germanous sulphide contained a trace of quadrivalent germanium, it was readily soluble in caustic alkali, an opaque red solution being obtained. If these solutions were centrifuged a considerable amount of germanous sulphide could be separated. Addition of dilute hydrochloric acid precipitated germanous sulphide completely, and precipitation was also brought about if ammonium chloride, ammonium carbonate, or potassium chloride was added to the solution. These facts all point strongly to the solutions being colloidal. These colloidal germanous sulphide solutions are readily oxidised, germanium disulphide and dioxide being formed. It was also found that if great care was taken to remove all quadrivalent germanium, and if precautions were taken against oxidation, then amorphous germanous sulphide was insoluble in caustic alkalis. It therefore seems probable that colloidal solutions in caustic alkalis were only formed in presence of germanium disulphide and dioxide. Both these compounds are soluble in alkalis, giving germanate and thiogermanate ions, these ions providing the charges needed to stabilize the colloidal germanous sulphide particles. It can therefore be stated that germanous sulphide resembles the oxide in showing no observable acidic properties.

Experimental.

A solution of germanium dioxide (0·25—0·5m.) was reduced by ½ hour's refluxing with excess of 30% hypophosphorous acid. The germanous hydroxide was then precipitated by addition of excess of ammonia solution, filtered off in a nitrogen atmosphere, and well washed with air-free distilled water.

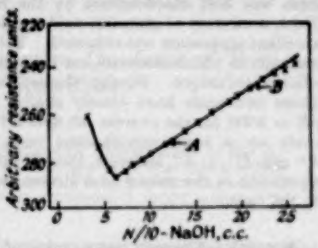
The solubility of germanous hydroxide was measured by addition of excess to about 100 ml. of air-free distilled water in a 250-ml. conical flask. A vigorous stream of oxygen-free nitrogen was then bubbled through the solution for about 15 minutes, after which the flask was carefully sealed, and placed in a thermostat at 25° for 24—30 hours, the flask being shaken at regular intervals. The excess of germanous hydroxide was then allowed to settle out, and 25-ml. samples of the supernatant liquid were carefully pipetted out and oxidised by addition of two or three drops of hydrogen peroxide (30 -vol.), and the germanium dioxide so formed was titrated as a monobasic acid after addition of glycerol (Tchakarian, *Compt. rend.*, 1928, **187**, 229). The results obtained, expressed as g. of germanous oxide (GeO) per 100 ml. of water, were as follows: 0·054, 0·033, 0·048, 0·033, 0·052, 0·058, 0·027, 0·051; mean, 0·044.

Acidic Properties of Germanous Hydroxide.—The conductivity experiments were carried out in a three-necked flask of about 500-ml. capacity; the two outside necks held the electrodes which were 2-cm. squares of bright platinum. Air-free distilled water (100 ml.) was then added, and a rapid stream of oxygen-free nitrogen was passed continously through the solution, ensuring that an inert atmosphere was present and also that the contents of the flask were well stirred.

To get pure germanous hydroxide, free from any quadrivalent germanium, some of the freshly precipitated compound was dissolved in about 5—7 ml. of concentrated hydrochloric acid. This solution was then evaporated to about half its original volume, any quadrivalent germanium distilling out as germanium tetrachloride (b. p. 83°). This purified solution was then poured into the water contained in the three-necked flask, whereupon hydrolysis took place and pure germanous hydroxide was precipitated. Alkali (0·1N.) was then run into the solution, and the change in conductivity noted. The minimum of the conductivity curves was taken as the point where all the hydrochloric acid had been neutralised; any reaction between the germanous hydroxide and the alkali would then start at that point. No solution of the germanous hydroxide was observed to take place even when ten times the theoretical amount of alkali had been added. There was also no trace of a break in the conductivity curve obtained (see figure). When a very vigorous stream of nitrogen was passed into the solution, a red opaque suspension was formed, but after a few minutes' standing all the germanous hydroxide had

settled out. The amount of germanium in the supernatant liquid was shown to be negligible by oxidising the solution by bubbling a stream of air through it, adding acid to give an acidity of 6N., and passing in hydrogen sulphide, but no germanium disulphide was precipitated. Subsequent experiments under the same conditions have shown that germanous hydroxide is insoluble in alkali up to 1N. in concentration if all quadrivalent germanium is absent; otherwise colloidal solutions tend to be formed.

Germanous Sulphide. All the preparations were carried out by passing hydrogen sulphide into a solution of bivalent germanium in hydrochloric acid (see preparation of germanous hydroxide). In the first method this solution was first neutralised with dilute ammonia, hydrogen sulphide passed in, and the resultant precipitate of germanous sulphide filtered off in a nitrogen atmosphere and then dried in a vacuum over phosphoric oxide, the desiccator having been filled with nitrogen before evacuation. Germanium was determined by oxidation with nitric acid to germanium dioxide, followed by ignition (Found: Ge, 72·69, 74·04, 71·40, 73·03. Calc. for GeS: Ge, 69·37%). The high results were traced to co-precipitation of germanous hydroxide owing to the fact that the solution had been neutralised with ammonia before passage of hydrogen sulphide. On drying, germanous hydroxide would give germanous oxide. These samples were all soluble in caustic alkalis, even after digestion for 24 hours with a few ml. of ammonia (*d* 0·880) to remove germanium disulphide. It was very probable that these samples contained germanium dioxide formed by oxidation of the germanous oxide. Germanium dioxide cannot be detected in presence of germanous sulphide by determination of only germanium, as the percentage of germanium is the same in both cases.



A and B represent the amounts of sodium hydroxide necessary to neutralise the first and the second hydrogen atom in germanous hydroxide.

The second method consisted of first saturating the bivalent germanium solution with hydrogen sulphide, adding dilute ammonia solution while the passage of hydrogen sulphide was continued till all the germanous sulphide had been precipitated, filtering this off, and drying it as before. Germanium was determined as before. Sulphur was determined by dissolving the germanous sulphide in alkali in presence of hydrogen peroxide; this solution was then boiled for about ½ hour, the sulphur being oxidised to sulphate, which was then precipitated as barium sulphate and ignited (Found: Ge, 69·19; S, 30·91. Calc. for GeS: Ge, 69·37; S, 30·63%). These results indicate that a very small amount of germanium disulphide was still present; it was observed that this sample was somewhat soluble in caustic alkalis, giving a colloidal solution. When this sample was digested for 24 hours in ammonia solution (*d* 0·880) to remove the last traces of germanium disulphide, it was found to be quite insoluble in alkalis. This was shown by placing the sulphide in air-free N-sodium hydroxide solution, and bubbling in a rapid stream of nitrogen to stir the solution and to ensure an inert atmosphere. After 2 hours no solution had taken place.

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468. *Amino-acid Separations by Use of a Strong-base Resin.*

By C. W. DAVIES, R. B. HUGHES, and S. M. PARTRIDGE.

The possible value of an ion-exchange resin of strong-base type in the separation of amino-acid mixtures has been studied. Good separations of leucine–glutamic acid and leucine–methionine mixtures have been effected

CONSIDERABLE success has been attained in the fractionation of amino-acid mixtures by means of ion-exchange resins of the strong-acid type (Partridge and Westall, *Biochem. J.*, 1949, **44**, 418; Partridge, *ibid.*, 1949, **44**, 521). The mechanisms operative in these separations have been discussed in the papers quoted and elsewhere (Davies, *ibid.*, 1949, **45**, 38). They depend on (*a*) the extent of ionisation of the individual amino-acids in their passage down the resin column, (*b*) the charges carried by the ions present, and (*c*) the van der Waals forces between the resin and the various species present. The relative importance of these effects can be controlled in a number of ways, by variation of the resin structure, of the nature of the liquid phase, and of the temperature, so that the versatility of the method is considerable. Improved separations resulting from a change of the developing solution (Partridge, *ibid.*, 1949, **45**, 459) and from an alteration of the temperature (Partridge, *ibid.*, in the press) have already been demonstrated; and a further possibility that is being explored is to utilise the strong tendency of the amino-acid anions to associate with bivalent metal cations.

The use of basic resins has, until recently, been severely restricted by the lack of strong-base exchangers. The earlier basic resins, which owed their exchange properties to amino- and imino-groups, have been successfully applied to the separation of the acidic from the neutral amino-acids, and to the separation of the acidic acids from one another (Consden, Gordon, and Martin, *ibid.*, **1948**, **42**, 443; Partridge and Brimley, *ibid.*, **1949**, **44**, 513); but they were quite unsuitable for use with the neutral amino-acids. The position has now been changed by the advent of strong-base resins of the quaternary-ammonium type, and the object of this short paper is to report preliminary measurements made by using one of these resins, Dowex 2. The resin was first characterised by the methods described by Partridge and Westall (*loc. cit.*). Next, a mixture of glutamic acid and leucine was separated on the regenerated column and an excellent separation was obtained. This pair of acids could, of course, be separated by the earlier methods to which reference has been made; but the use of a strong-base resin gives an equally efficient technique. Finally, the separation of a mixture of leucine and methionine was tested. These two acids have closely similar dissociation constants (leucine $pK = 2{\cdot}36$, methionine $pK = 2{\cdot}28$) for the process $A^+ \rightleftharpoons H^+ + A^\pm$, and in the fractionation of a mixture of amino-acids on a negatively-charged resin they appear in the same band. For the process $A^\pm \rightleftharpoons H^+ + A^-$, however, the pK values are: leucine, 9·60, and methionine, 9·21, so that the separation of the anions on a strong-base resin should be relatively simple. This was found to be the case.

Experimental.

Materials.—The resin was a sample of Dowex 2 graded to 250—500 mesh. It was in the form of cream-coloured micro-beads, and was supplied as the chloride. It was regenerated with carbonate-free sodium hydroxide until chloride-free, and washed with carbonate-free distilled water until the alkalinity of the eluate fell to below pH 8. The importance of having all solutions carbonate-free cannot be over-emphasised. If any carbonate becomes adsorbed on the resin, carbon dioxide will be released by the eluting acid and will seriously disturb the chromatogram.

AnalaR hydrochloric acid and acetic acid were used, being diluted as required with carbonate-free distilled water. The amino-acids were laboratory reagents.

Characterisation of the Resin.—By utilising the method described by Partridge and Westall (*loc. cit.*) values for λ_{90} (the boundary width in cm.) and ε (the capacity in millimols. per g. of dry resin) were obtained. Four runs were carried out with hydrochloric and acetic acids. The concentrations of the acids and the rate of progression of the boundary (S) were varied as indicated. For these experiments a column 10·7 cm. high and 1·5 cm. in diameter was used, containing 8·4 g. of the resin. The results obtained are shown in the Table.

Acid.	Concn. (g.-equiv./l.).	S (cm./hr.).	λ_{90}.	ε.
Hydrochloric	0·108	2	0·96	3·73
Hydrochloric	0·205	4	1·38	3·63
Acetic	0·106	4	2·13	3·67
Acetic	0·249	2	1·92	3·71

The boundaries are wider than those obtained with Zeo-Karb 215 (Partridge and Westall, *loc. cit.*) in spite of a lower boundary progression rate. The wider boundaries for acetic acid, compared with hydrochloric acid, may be due to van der Waals adsorption of the acid molecules. The values obtained for ε show that the resin behaves unifunctionally over the pH range studied.

The Separation of Leucine and Glutamic Acid.—For the experiments on the separation of amino-acids a second, smaller column of resin was fitted beneath and in series with the column used in the characterisation experiments. This smaller column contained 2·9 g. of resin, and was 8 cm. high and 1 cm. in diameter. The two columns were operated as a single unit.

5 Millimols. each of leucine and glutamic acid were dissolved in 100 ml. of carbonate-free distilled water and run on to the regenerated and washed column. The adsorbed band occupied about one-third of the length of the column. The amino-acids were displaced with 0·1*N*-hydrochloric acid, the rate of flow being adjusted so that the amino-acid boundary, which was plainly visible, travelled down the larger column at a rate of 1·5 cm./hr., and down the smaller column at a rate of 2 cm./hr. As the boundary approached the bottom of the lower column, 5-ml. fractions of the eluate were collected; this was continued until the eluate gave a positive reaction for chloride. A spot from each fraction was analysed by the paper chromatographic method described by Consden, Gordon, and Martin (*Biochem. J.*, **1944**, **38**, 224). Glutamic acid could only be detected in the last of the fourteen leucine fractions, and only the first fraction of the glutamic acid band contained leucine.

The Separation of Leucine and Methionine.—The experimental procedure was identical with that described for the separation of leucine and glutamic acid, and similar quantities of the two acids were used. As the displacement proceeded, a band of insoluble material was seen to form immediately in front of the hydrochloric acid boundary. To prevent this blocking up the column the rate of displacement had to be increased considerably above that of the previous run. In spite of this a good separation was obtained, and only four out of the twenty-four amino-acid fractions contained mixed acids. The paper chromatogram indicated that the insoluble material was cystine, which frequently occurs as an impurity

in commercial methionine. As the cystine became concentrated into a band its low solubility was exceeded, and crystals separated out in the column.

We thank the Dow Chemical Company, of Midland, Michigan, U.S.A., for the sample of Dowex 2 used in this work.

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469. *The Determination of the Dissociation Constants of Very Sparingly Soluble Weak Electrolytes.*

By R. N. BEALE and A. LIBERMAN.

A differential method is proposed for the spectrophotometric determination of the dissociation constants of very sparingly soluble electrolytes, which is applicable where the solubility of the un-ionised compound is so low that its absorption spectrum cannot be determined.

The method has been tested and confirmed for 4-dimethylamino-2'-methylstilbene, the solubility of which (in water) is $\sim 2 \times 10^{-6}$M.

DURING investigations of the physicochemical properties of a series of carcinogenic aminostilbene derivatives, requiring determination of their dissociation constants, it immediately became apparent that direct potentiometric titration or conductance measurements would fail completely owing to the low solubilities in water (*ca.* 10^{-4}M.)

Other methods have been proposed, *e.g.*, titration with perchloric acid in glacial acetic acid (Hall and Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 3047, 3062) or titration in aqueous organic solvents, in which the solubility of the base is somewhat higher than in water (Albert and Goldacre, *Nature*, 1942, **149**, 245; Bell and Roblin, *J. Amer. Chem. Soc.*, 1942, **64**, 2905; Kumler and Daniels, *ibid.*, 1943, **65**, 2190; Stockton and Johnson, *J. Amer. Pharm. Assoc.*, Sci. Ed., 1944, **33**, 383; Cook, Heilbron, Reed, and Strachan, *J.*, 1945, 861). The method used by Cook *et al.* (*loc. cit.*) was not applicable for all the compounds which they investigated. Furthermore, extrapolation of data obtained by these methods to pure aqueous solutions has been shown (Gorvin, *J.*, 1949, 3309) to be unreliable. A considerable number of dissociation constants of bases, reported by Hall and Sprinkle (*J. Amer. Chem. Soc.*, 1932, **54**, 3469), were obtained from e.m.f. measurements of a concentration cell containing the half-neutralized base. This method, however, is not applicable to aminostilbene derivatives, because of their low solubilities and because hydrolysis and other corrections would be of such a high order as to render the results of doubtful accuracy. Krebs and Speakman (*J.*, 1945, 593) have proposed a method for slightly soluble bases depending on the solubility at a number of pH values. The method is limited by three factors: (*a*) the base should be capable of being determined in the presence of the buffer solution; (*b*) the limiting solubility of the base must not be immeasurably small; in the example quoted (sulphadiazine), it was of the order of $2{\cdot}5 \times 10^{-4}$M.; (*c*) the electrolyte should not decompose in the solutions employed during the time taken to reach equilibrium (cf. dithizone; Irving, Cooke, Woodger, and Williams, *J.*, 1949, 1847).

Spectrophotometric techniques have been used for the determination of the dissociation constants of organic compounds in the visible (Brode, *J. Amer. Chem. Soc.*, 1924, **46**, 581; Holmes and Snyder, *ibid.*, 1925, **47**, 2232), and in the ultra-violet region (*inter alii* Flexser, Hammett, and Dingwall, *ibid.*, 1935, **57**, 2103; Clark, "The Determination of Hydrogen Ions," MacMillan and Co., 3rd Edition, 1928). In all of these a knowledge of the extinction coefficients both of the ion and of its conjugate base at a number of wave-lengths is necessary. Such spectrophotometric methods are particularly suitable for solutions of low concentrations (10^{-4}—10^{-5}M.) if $\epsilon_{max.}$ is large, (*e.g.*, $\sim 10^4$, 1-cm. cell). It was considered possible, therefore, to apply the methods to the sparingly soluble aminostilbenes which absorb strongly in the ultra-violet region. However, because of the immeasurably small limiting solubility in water of the free bases, it was found impossible to measure their absorption spectra, even in a cell of 5-cm. light path. It was therefore necessary to devise an alternative procedure, taking advantage of the greater solubility of the ion at lower pH values.

For substances which obey Beer's law, the usual spectrophotometric determination of dissociation constants (Clark, *op. cit.*, p. 154) consists in measuring, at a particular wave-length, the optical density of absorption of a series of solutions of known total concentration with different

pH values. If α is the degree of *ionisation* of the base in any one of these solutions, then the observed optical density D is given by the equation

$$D = \epsilon_a lc\alpha + \epsilon_b lc(1-\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ϵ_a and ϵ_b are respectively the molar extinction coefficients of the ion and of the base, c is the molar concentration, and l the cell-length in cm.; ϵ_a and ϵ_b are previously determined by measurements of solutions of known concentration and of sufficiently high and low pH values, where α is virtually zero and unity respectively (for a base). Equation (1) then reduces to

either $$D_a = \epsilon_a lc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

or $$D_b = \epsilon_b lc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

It follows that (1) may also be written as

$$D = D_a\alpha + D_b(1-\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

It is frequently possible to find a suitable wave-length at which ϵ_a or ϵ_b is zero, and this is the normal practice. One of the terms on the right-hand side of (1a) then disappears and α is immediately determinable. In the present work, ϵ_b, as previously indicated, could not be determined; and for no wave-length can it be certain that absorption of light is due to the ion only, so that (1a) cannot be applied directly. It is possible, however, to determine α at any suitable pH value by the following procedure, involving a knowledge of the extinction coefficient of one species only.

Consider a base ionizing according to

$$BH^+ \rightleftharpoons B + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Then application of the law of mass action and rearrangement gives

$$pK_a = pH + \log \alpha/(1-\alpha) - \log f_{BH^+}/f_B \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$pK_a' = pH + \log \alpha/(1-\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where f refers to an activity coefficient and K_a' is Brønsted's acidity constant (*Chem. Reviews*, 1928, **5**, 293).

At two values of the hydrogen ion activity $\{H^+\}_1$ and $\{H^+\}_2$, measured by pH_1 and pH_2, it follows from (5) that

$$\Delta pH = pH_1 - pH_2 = \log \frac{\alpha_2(1-\alpha_1)}{\alpha_1(1-\alpha_2)} = \log R_H \text{ (say)} \quad . \quad . \quad . \quad . \quad (6a)$$

Then $$R_H = \alpha_2(1-\alpha_1)/\alpha_1(1-\alpha_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6b)$$

and from (6a) $$R_H = \{H^+\}_2/\{H^+\}_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From (6b) also, $$\alpha_1 = \alpha_2/[R_H + (1-R_H)\alpha_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For any wave-length we have, from (1a):

At pH_1, $$D_1 = D_a\alpha_1 + D_b(1-\alpha_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

At pH_2, $$D_2 = D_a\alpha_2 + D_b(1-\alpha_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

whence $$(D_1 - D_a\alpha_1)/(D_2 - D_a\alpha_2) = (1-\alpha_1)/(1-\alpha_2) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From (8) and (11) it can be shown that

$$\alpha_1 = (D_1 - D_2)/(D_a - D_2)(1-R_H) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\alpha_2 = (D_1 - D_2)R_H/(D_a - D_1)(1-R_H) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

From (7), (12), and (13) it follows that

$$\alpha_1 = \frac{D_1 - D_2}{D_a - D_2} \cdot \frac{\{H^+\}_1}{\{H^+\}_1 - \{H^+\}_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

$$\alpha_2 = \frac{D_1 - D_2}{D_a - D_1} \cdot \frac{\{H^+\}_2}{\{H^+\}_1 - \{H^+\}_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

Substitution of α from (12) or (13) in (5), the appropriate pH value being used, gives the value of pK_a'.

Experimental.

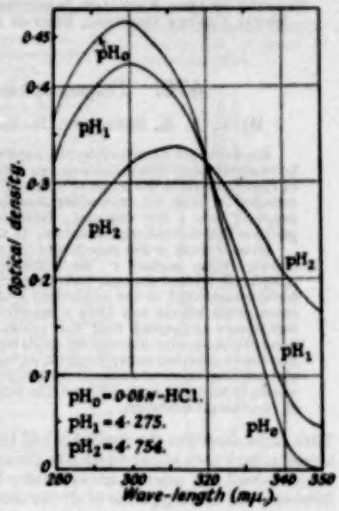
The procedure was used for the determination of the dissociation constant of 4-dimethylamino-2'-methylstilbene. Measurements of optical density were made on the "Uvispek" spectrophotometer adapted to take 5-cm. Beckman cells. Thermostatic control was not attempted, although the temperature of the room was maintained as nearly as possible at 20° ±1°. Measurements of pH were made with the glass electrode standardised with potassium hydrogen phthalate, and the temperature thermostatically controlled at 20° ±0·2°, in well-buffered solutions, over the range required.

The pure 4-dimethylamino-2'-methylstilbene, previously synthesised in this Institute, was recrystallised from light petroleum (b. p. 40—60°) immediately before use, and sufficient was dissolved in N-hydrochloric acid to give a final concentration of approximately 2×10^{-4}M.

Equal aliquot portions of this solution were added to suitable amounts of N-hydrochloric acid and of M-sodium acetate, and the whole diluted so that the total concentration of the stilbene was of the order of 4×10^{-5}M. at the required pH value. The solution was also maintained at an ionic strength $I = 0{\cdot}05$ by suitable additions of 0·1M-sodium chloride.

For measurement of the optical density of absorption of the ion (D_s), an aliquot was taken and added to sufficient hydrochloric acid so that on dilution the final acid concentration was 0·05N. After optical measurements of the buffered solutions the pH values of the cell contents were taken.

In the earliest experiments anomalous absorption spectra were obtained. This was thought to be due to adsorption of positive stilbene ions on the fused quartz walls of the cells (which would seriously affect solutions of such low concentrations), because this effect was particularly noticeable after cleaning the cells with chromic–sulphuric acid, even after prolonged washing with water. It was inferred that the cell walls were still negatively charged, and that the neutralization or reversal of this charge by use of a cationic detergent would lead to more consistent results. Therefore, the cells were rinsed with 0·01% aqueous trimethylcetylammonium bromide, followed by thorough washing with distilled water. After such "lining" of the cell with a detergent multilayer, the stilbene solutions were found to obey Beer's law at any pH value, and it was concluded that this treatment was sufficient to inhibit the adsorption of the positive stilbene ions.



In the figure are shown the absorption spectra of the basic stilbene in 0·05N-hydrochloric acid and in acetate buffers at pH 4·27$_4$ and pH 4·75$_4$. The accuracy of any experiment may be gauged by the concurrence of the spectra at the isobestic point, the wave-length at which the extinction coefficients of the base, its ion, or any mixture of the two, are equal. In the figure, the isobestic point is seen to be at 321 mμ. (See Clark, *op. cit.*, pp. 153, 687.)

In another experiment, in which additions of the cationic detergent at a concentration of 1 in 10^7 were made, very good agreement was obtained; an identical isobestic point was found. The table summarises the results obtained in a typical experiment.

Spectrophotometric determination of dissociation constant of 4-dimethylamino-2'-methylstilbene.

λ (mμ.).	D_0.	D_1.	D_2.	a_1.	a_2.	λ (mμ.).	D_0.	D_1.	D_2.	a_1.	a_2.
350	0·002	0·046	0·165	0·848	0·446	300	0·465	0·422	0·3175	0·823	0·392
345	0·008	0·057	0·184	0·838	0·418	295	0·450	0·412	0·296	0·827	0·398
340	0·0395	0·0855	0·2085	0·845	0·432	290	0·443	0·394	0·272	0·829	0·402
335	0·108	0·145	0·244	0·845	0·432	285	0·413	0·365	0·242	0·835	0·414
330	0·182	0·207	0·275	0·849	0·439	280	0·367	0·323	0·209	0·838	0·418
305	0·451	0·416	0·330	0·825	0·397	—	—	—	—	—	—
										Means	0·826	0·417
											±0·010	±0·018

Mean $pK_a' = 4{\cdot}59 \pm 0{\cdot}03$.

A series of experiments with the same compound gave a mean value for pK_a' of 4·58 ± 0·04 at 20°. As previously mentioned, the solutions were of ionic strength $I = 0{\cdot}05$ for all experiments. With the conventional assumption that the activity coefficient of the un-ionised base is unity, the calculation of the mean activity coefficient of the ion is given with sufficient accuracy from the approximate Debye-Hückel equation $-\log f_{BH^+} = 0{\cdot}502 z_i \sqrt{I}/(1+\sqrt{I})$. For the uni-univalent electrolyte employed, this gives $-\log f_{BH^+} = 0{\cdot}09$. Hence the thermodynamic pK_a is 4·67 ± 0·06 at 20°.

The treatment has been confined to a sparingly soluble monoacid base, but it is clear that with suitable modification it can equally well be applied to a monobasic acid. It is also possible that this method may find application in cases where, although the limiting solubility of the compound is higher, it is nevertheless unstable in acid or alkaline medium.

This investigation has been supported by grants to the Royal Cancer Hospital from the British Empire Cancer Campaign, the Jane Coffin Childs Memorial Fund for Medical Research, the Anna Fuller Fund, and the Research Grants Division of the United States Public Health Service. Our thanks are offered to Dr. E. M. F. Roe for her interest in the work, and we acknowledge the assistance of Mr. F. C. Middleton in some of the spectrophotometric measurements.

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470. *Polymorphism in Tetraethyl-tin and -lead.*

By L. A. K. STAVELEY, H. P. PAGET, B. B. GOALBY, and J. B. WARREN.

Experiments on tetraethyltin, carried out on different samples in three types of apparatus, have shown that this substance can crystallise in at least ten forms. The melting points of all of these lie within the range 137° to 148° K. A less complete investigation of tetraethyl-lead has revealed at least six crystalline modifications, the melting points of which likewise fall in a range of only a few degrees. Tetramethyl-tin and -lead, however, and also 3 : 3-diethyl-*n*-pentane and tetraethylgermanium, do not show polymorphism of this kind.

Even if there is free rotation of the methyl groups in a particular tetramethyl molecule, the corresponding motion in the tetraethyl molecule is impeded by steric interference of the peripheral methyl groups, and moreover the freedom of movement of these groups must be further restricted in the condensed states by intermolecular interlocking. The magnitude of these steric effects will have a sensitive dependence on the size of the central atom. It is tentatively suggested that the unusual polymorphism of tetraethyl-tin and -lead results from the molecular dimensions enabling the molecules to pack into different lattices in which they have different configurations, so that interaction between the methyl groups of a molecule, and between those of adjacent molecules, differs from one crystalline form to another. In other words, in the solid state, at least, the molecules of these two polyalkyl compounds exhibit a form of rotational isomerism.

THIS paper describes the discovery and the investigation of an uncommon type of polymorphism, a preliminary note about which has already been published (*Nature*, **1949**, **164**, 787) : tetraethyl-tin and -lead can exist in an unusually large number of crystalline forms. For each of these, however, the melting points of all the modifications fall within a few degrees. The phenomenon was discovered with tetraethyltin, and has been more fully investigated for it than for tetra ethyl-lead. On the other hand, experiments with tetramethyl-tin and -lead and " tetra-ethylcarbon " (3 : 3-diethyl-*n*-pentane) gave no indication of more than one melting point, and preliminary observations on tetraethylgermanium suggest that this is true of this substance also. The comparison suggests that the ability of tetraethyl-tin and -lead to crystallise in a large number of different forms is a property which has a very sensitive dependence on molecular structure. This will be discussed further after the experimental facts have been presented.

EXPERIMENTAL.

Three series of experiments on tetraethyltin were carried out. The observations in series I were made with the low-temperature calorimeter described by Staveley and Gupta (*Trans. Faraday Soc.*, 1949, **45**, 50), those of series II in an apparatus constructed of glass so that the crystallisation and melting could be observed, and those of series III in an apparatus similar to that designed at the U.S. Bureau of Standards for the accurate measurement of m. p.s below room temperature (Mair, Glasgow, and Rossini, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 591).

Temperature measurements in series I were made with a platinum resistance thermometer wound on the calorimeter and calibrated *in situ* against methyl bromide, methyl chloride, phosphine, ethylene, and methane vapour-pressure thermometers, the calorimeter itself serving as the bulb for the liquid.

The glass apparatus in which series II was carried out in shown in Fig. 1 M. p.s were measured with a built-in ethylene vapour-pressure thermometer. The vessel 1 which contained the alkyl had a capacity of about 10 c.c. and surrounding this in 2 was the liquid ethylene. The copper wire spiral 3 provided for uniformity of temperature in the ethylene jacket and also prevented bumping of the liquid during evaporation. The dimensions of 2 were such that some of the ethylene could be evaporated in order to cool vessel 1 and its contents, whilst sufficient remained for the temperature of the alkyl compound to be read accurately. The space 4 was evacuated, or, alternatively, hydrogen was admitted into it when thermal contact between 1 and 2 and the surroundings was necessary. The apparatus was immersed in a low-temperature thermostat, consisting of a 2-l. Dewar vessel with an unsilvered stripe down the side so that the tetraethyltin could be kept under observation. The thermostat was filled with *iso*pentane,

which was stirred by a rotating glass helix and kept at a constant temperature by the transference, at a controlled rate, of liquid oxygen into a copper tube in the bath-fluid. The temperature of this was determined with a separate ethylene vapour-pressure thermometer. The ethylene vapour pressures were read to 0·2 mm., which in the range in which the numerous m. p.s of tetraethyltin fall represents an accuracy of 0·02°.

The ethylene was prepared from absolute ethyl alcohol and syrupy phosphoric acid (Klemenc, "Die Behandlung und Reindarstellung von Gasen," Leipzig, 1938). Acid vapours were removed by concentrated aqueous potassium hydroxide, and alcohol vapour by a trap filled with glass-wool and cooled by solid carbon dioxide–acetone. The ethylene was condensed as solid in a trap cooled by liquid oxygen. It was purified by fractional distillation in a column of the type described by Clusius and Riccoboni (*Z. physikal. Chem.*, 1939, **38**, *B*, 81), the column being kept at an average temperature of −127° in a bath of ether and alcohol cooled by the passage of liquid oxygen through a copper spiral. In the calorimeter used for series I, the m. p. of a sample of ethylene prepared in this way changed by only 0·011° between 20 and 80% melted.

FIG. 1.

All-glass apparatus used for experiments of series II on tetraethyltin.

The apparatus employed in series III was designed to operate with a charge of about 20 c.c. of liquid. Temperatures were determined with a relative accuracy of 0·02° with 3-junction copper–constantan thermocouples. These had been calibrated and were frequently checked in the same apparatus at the f. p.s of mercury, chloroform, *n*-heptane, and carbon disulphide, and also in liquid air the temperature of which was measured with a carbon monoxide vapour-pressure thermometer. The values of the E.M.F. at the five known temperatures were then used to construct a deviation curve from the data given by Southard and Andrews (*J. Franklin Inst.*, 1929, **207**, 323).

Tetraethyltin.—Several samples were used. All were prepared from stannic chloride and ethyl-magnesium bromide (Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Berlin, 1937, p. 315). According to these authors, this is the method best suited to the small-scale preparation of tin alkyls. Made in this way, the crude product usually contains triethyltin chloride. In the preparation of the sample used in series I (sample *A*), this chloride was removed by agitating the ethereal solution with aqueous-alcoholic potassium fluoride and filtering off the insoluble triethyltin fluoride. After removal of the ether, the tetraethyltin was dried over phosphoric anhydride and distilled at atmospheric pressure. It was then fractionated in an all-glass apparatus under reduced pressure, and the middle fraction refractionated under the same conditions (b. p. 39·5°/2 mm.). The middle cut from this process was stored over phosphoric anhydride until required, when it was degassed and condensed into the calorimeter. The following figures, indicating the purity of sample *A*, represent the temperatures recorded at different stages of the melting of the crystalline form later designated as *d*:

% melted	37·9	44·2	57·5	65·5	72·1
T (° K.)	140·44°	140·51°	140·52°	140·53°	140·54°

If the impurities are regarded as liquid-soluble but solid-insoluble, these figures lead, by conventional methods, to m. p. 140·56° for the actual sample and to m. p. 140·61° for the pure substance. This corresponds to an impurity concentration of 0·25 mole-%. It may be added that anomalously high heat-capacity values, caused by premelting, were not observed until the temperature was within 4° of a m. p.

Two new samples *B* and *C* were made for the experiments of series II. Sample *B* was purified by aqueous-alcoholic potassium fluoride as for *A*, and the crude specimen was fractionated under atmospheric pressure in an all-glass apparatus, the fraction of b. p. 175—177° being collected. This was then refractionated at 26·5 mm. (b. p. 93·5°). In a test for halides, a sample of the distillate was refluxed with aqueous sodium hydroxide and, after acidification, gave no precipitate with silver nitrate solution. The resulting sample *B* was dried over phosphoric anhydride, degassed, and distilled into the apparatus *in vacuo*.

Sample *C* was freed from halides by an alternative procedure described by Krause and von Grosse (*op. cit.*), namely, by passing dry ammonia through the dry ethereal solution of the alkyl until no more precipitate (a double compound of the triethyltin halide with two moles of ammonia) appeared. The precipitate was filtered off and the ethereal solution dried ($CaCl_2$). After removal of the ether, the crude tetraethyltin was distilled twice at atmospheric pressure, the fraction of b. p. 175—177° being nearly the entire sample. This was then fractionated under reduced pressure and the middle fraction collected. A halide test at this point proved entirely negative. However, when it was cooled to −125°, an unidentified white substance was precipitated. This was filtered off at this temperature, and the liquid refractionated under reduced pressure. The product was Sample *C*, which was kept over phosphoric anhydride and then vacuum-distilled into the apparatus.

The glass apparatus in which the experiments of series II on samples *B* and *C* were conducted was primarily designed to permit observation of the crystallisation and melting, and was not ideally suited to the precise determination of m. p.s. Moreover, as will be described more fully later, in this apparatus the substance tended to crystallise in several forms simultaneously rather than largely in one. This made it difficult to assess the purity of the samples used in series II from the melting curves, but at least

there appeared to be satisfactory agreement between the corresponding figures obtained with the two samples *B* and *C*. Thus m. p.s were found at : 145·75° K. for *B*, and at 145·8° ± 0·1° for *C*; at 143·1° for *B* and at 143·15° for *C*; at 142·1° ± 0·1° for *B* and *C*.

Sample *D* used in series III consisted of samples *B* and *C*, together with a new portion from which the halide impurities had been removed by treatment with ammonia, as for sample *C*. The mixture was dissolved in dry ether and again treated with ammonia. The product was then twice fractionated in a 12-plate column, the middle fractions being collected. Sample *D* had d_4^{20} 1·1913, and n_D 1·4719 at 20°, 1·4702 at 23°, and 1·4696 at 25°. The results are in excellent agreement with those obtained by Kőrösching (*Z. Naturforsch.*, 1946, **1**, 219) on a carefully purified sample (d_4^{20} 1·1916, n_D^{20} 1·4717, n_D^{25} 1·4693).

Tetraethyl-lead.—A sample of this substance was obtained from the Associated Ethyl Company. It was stated to be of high purity and was used without any further treatment. While the experiments carried out on this substance have sufficed to show that it also exists in several crystalline forms it appeared that the purity of the material used deteriorated gradually under the experimental conditions, perhaps owing to oxidation, and it is intended to re-investigate the melting phenomena with more highly purified specimens.

Results for Tetraethyltin.

Series I.—In these experiments crystallisation never occurred until the substance had been considerably supercooled. The usual procedure was to supercool the substance by about 30° and then to heat it electrically. A sudden increase in the rate of temperature rise indicated that crystallisation had started, but sometimes the cooling and heating had to be repeated several times before this happened. Crystallisation generally began about 25° below the temperature at which most of the solid later melted. Once crystallisation had commenced the electrical heating was stopped and the temperature allowed to rise of its own accord. Then the sample was re-cooled, and a run carried out by heating it electrically and taking time–temperature readings while maintaining adiabatic conditions throughout. Sometimes the sample was heated continuously, until it was all liquid, with the object of carrying out the run as quickly as possible and thereby reducing the chance of any recrystallisation or interconversion of the various forms. In such experiments thermal equilibrium between the walls of the calorimeter and its contents was not properly established, and the arrests in the corresponding temperature–time curves are inclined and not horizontal. In other experiments, heating was periodically interrupted during melting and the calorimeter allowed to attain a steady temperature.

On three occasions the liquid crystallised spontaneously on cooling, when the temperature had fallen to approx. 120° K. In two of these experiments this resulted in the production of the form with the lowest melting point observed in this series (form *a*).

Some 20 experiments in all were carried out. Temperature–time curves for 8 of these are plotted in Fig. 2, which between them indicate at least five different m. p.s. The temperatures of arrests in the remaining experiments, not represented in Fig. 2, were all consistent with one or other of these 5 m. p.s.

As we do not consider that we have necessarily measured *all* the m. p.s which this substance possesses, we shall not follow the usual practice of designating the polymorphic forms I, II, III, etc., in order of decreasing m. p. Instead the different forms will be provisionally labelled *a*, *b*, *c*, etc., in the order in which they are described.

The modification (*a*) of lowest m. p. was obtained in two experiments only, both of which were carried out early in the investigation, before the complexities of the system had been fully realised. While neither was conducted in the manner best suited to a precise m. p. determination the m. p. of *a* can be given with reasonable precision as 138·1° ± 0·1° K. Form *b* appeared on 5 occasions, but never alone or in sufficient quantity for accurate observation. The data are, however, consistent with m. p. 138·7° ± 0·2° K. The presence of modification *c* was revealed in 6 experiments, in all of which it was accompanied by one or two of the other forms. From a run in which it formed the major part of the crystals and which was carried out with intermittent heating the m. p. of *c* was estimated to be 139·80° ± 0·05 K. Form *d* appeared 4 times, and once was unaccompanied by any other modification; from this run, the value obtained for the m. p. of *d* was 140·61° K.

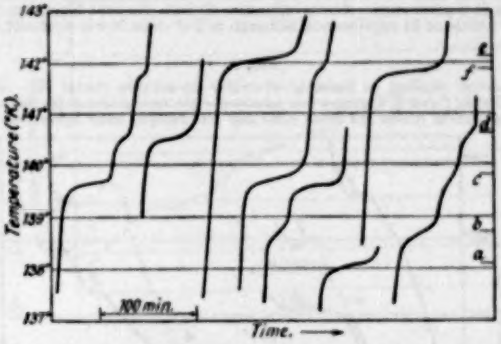
The form most frequently produced in series I was that with the highest m. p. This form *e* was obtained in 7 experiments and in 4 of these was the only form present. If a heating run indicated the presence of *e* after any other forms had melted, then if the temperature was reduced a little just after the fusion of *e* had started the whole sample crystallised out in this modification. Its m. p. was 142·12° K. In 5 runs it seemed that a form *f*, with a slightly lower m. p. than that of *e*, had appeared, for which a m. p. of 141·87° K. was obtained (cf. the 4 curves in Fig. 2 which indicate melting in the neighbourhood of 142°). Unfortunately the position was complicated by a change, during the experiments, of the characteristics of the platinum thermometer. The resistance of this thermometer (which was wound on the calorimeter) increased, suggesting that the wire had been stretched owing to strain on the calorimeter walls. (In one experiment in series II the glass vessel containing the alkyl compound was shattered by the strain set up on crystallisation.) Fortunately, this change in the thermometer, which happened suddenly, did not occur until the existence of the four forms *a*—*d*, and of either *e* or *f*, had been established. We regard the existence of the two forms *e* and *f* (rather than that of one form *e* only) as probable, but not proven, and for this reason in our preliminary note (*loc. cit.*) only one form was stated to melt in the neighbourhood of 142° K., and a mean value of 142·05° K. for the m. p. was adopted.

The conclusion that all the arrests in the temperature–time curves of series I did in fact represent melting and that none could be connected with transitions was reached by a quantitative consideration of these curves assisted by a direct determination of the heat of fusion of form *e*. As this conclusion was amply confirmed by the experiments of series II and III, the argument need not be given in detail here. In addition to the heat of fusion of *e*, the heat capacities of the liquid alkyl compound and of the solid

crystallised in different ways were also measured. Owing to a slight uncertainty in the mass of the alkyl compound in the calorimeter the publication of these results will be withheld until further experiments have been completed. Three facts may be provisionally stated, however. First, that the entropy of fusion of form *e* is approximately 15 cals./g.-mol./degree, *i.e.*, of a magnitude which makes it unlikely that for this form at least there are any transitions with at all large entropy changes. Secondly, there is reason to believe that the heat capacities of the different forms may differ considerably. Thus that of form *d* just below its m. p. appears to be about 4 kcals./g.-mol. less than that of *e*. Lastly, there is a very considerable difference between $C_{p\,(\text{solid})}$ and $C_{p\,(\text{liquid})}$ at the m. p.s. For form *e*, C_p increases on melting by about 16 kcals./g.-mol. (Experiments in this laboratory have shown that for tetramethyltin this increase is about 10 kcals./g.-mol., for tetramethyl-lead about 7 kcals./g.-mol., and for 3 : 3-diethyl-*n*-pentane almost nil.)

FIG. 2.

Temperature–time curves obtained on warming crystalline tetraethyltin (series I). The letters on the right-hand side refer to the various solid modifications, and the small lines give the corresponding melting points.



Series II.—The experiments of this series were planned so as to vary as far as possible the conditions under which the substance crystallised. To cool the substance rapidly the apparatus was surrounded by liquid oxygen, with hydrogen in the outer space 4 (Fig. 1). Slower cooling was achieved either by using liquid oxygen and evacuating the outer space 4, or, with the vessel in the thermostat and the outer jacket evacuated, by evaporating liquid ethylene from space 3 by condensation into a cooled trap. Once the substance had been crystallised the thermostat was brought to a constant temperature a few degrees above the highest m. p., and temperature–time readings were taken as the solid warmed. During this process the outer space 4 was evacuated if it was desired that the warming rate should be as small as possible. Under these conditions complete melting took about 4—5 hours. To produce greater rates of warming a trace of hydrogen was admitted into 4 : a run could then usually be covered in an hour. Occasionally a run was started with the space 4 evacuated, and after melting had begun, hydrogen was admitted to 4 and then pumped away after substantially more of the solid had melted.

The substance was more reluctant to crystallise in this apparatus than in either of the other two, presumably owing to the absence of the stirring employed in the experiments of series III, and because the enclosing glass surfaces were much smoother than the walls of the calorimeter used in series I. On one occasion the alkyl compound remained as a glass for over 70 hours before attempts to crystallise it by varying the temperature succeeded. Once the formation of crystals had started, however, it proceeded throughout the whole mass rapidly, sometimes in a matter of seconds. Crystallisation usually started at the top or the bottom of the tetraethyl compound and transformed the glass into a mass of interlocking, apparently needle-like crystals. By varying the thermal treatment of the alkyl compound it was found that crystallisation was induced most easily by cooling it rapidly with liquid oxygen and then allowing it to stand. On only two occasions did crystallisation occur on warming of the vitreous solid. In one of these two experiments this caused the containing vessel to break. The warming run in the other experiment was the only one in series II in which the crystals melted completely in the temperature range convering the m. p. of series I. All other crystallisations of series II produced forms with higher m. p. than any we had hitherto recorded.

In two experiments melting was stopped before fusion was complete and the substance recooled. This, as was to be expected, induced rapid crystallisation, mainly into that form with which the melt had been seeded.

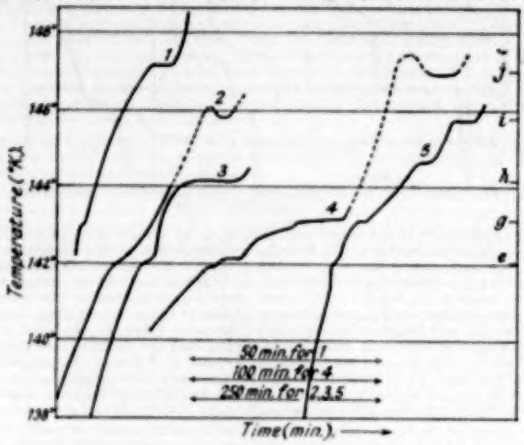
On 2 occasions, as soon as crystallisation started, the outer space 4 (Fig. 1) was rapidly evacuated and the solid and the liquid were left to come to a steady temperature. This proved to be much lower than the melting temperatures later recorded when the sample was subsequently recooled to complete crystallisation and then allowed slowly to warm. We shall later describe another experiment (in series III) in which the steady freezing and melting temperatures in the same experiment were definitely different.

In the later stages of the melting process in any one experiment, the remaining solid was, of course, at the bottom of the vessel, while heat was being communicated from the thermostat down the glass tubes at the top. This must have tended to cause the upper layers of liquid alkyl compound, and hence of the surrounding liquid ethylene, to have a higher temperature than the solid alkyl compound, and accordingly some ambiguity may attach to the interpretation of any steady temperatures recorded when most of the crystals had melted.

In all, 13 temperature–time curves for the fusion of the crystalline solid were determined in series II. Five of these are plotted in Fig. 3. Again it will be seen that there is a correspondence between the temperatures of arrest in these curves, which can scarcely be fortuitous. The lowest m. p. represented in Fig. 3 appeared in at least 5 experiments as an arrest in the temperature–time curve which always coincided with the first appearance of liquid. In 2 other experiments there was a small kink in the curve at this temperature, again coincident with the first visible signs of melting. The temperature corresponding to this arrest was 142·1° ± 0·1° K., and the crystal form involved would therefore appear to be identical with *e* of series I. The next form *g* was present on at least 3, and possibly 4, occasions, and was assigned m. p. 143·15° ± 0·05° K. In one experiment there was an arrest for over an hour at 144·1° ± 0·15° K. and there was evidence that the form (*h*) responsible for this had constituted part of the crystal mass in 2 other runs. The modification (*i*) with the next highest m. p. appeared more frequently, in 6 of a total of 13 experiments, although in 2 of these it was produced by seeding from a

FIG. 3.

Temperature–time curves obtained on warming crystalline tetraethyltin (series II). In the experiments represented by curves 2 and 4, hydrogen was admitted to the outer jacket at the stages represented by the dotted lines after partial fusion had taken place and was pumped away before melting was complete.



previous run. All 6 m. p. values were consistently 145·80° ± 0·05° K. Finally, on 5 occasions a form *f* with a still higher m. p. (147·1° ± 0·15° K.) was present. There was slightly more variability in this m. p. than in the others, presumably because there was relatively little solid remaining in the vessel by the time this arrest was reached.

The temperature–time curves sometimes showed small arrests at other temperatures. In curve 5 of Fig. 3, for example, there appears to be an arrest at 144·6°. It may be that these are evidence of the existence of yet other forms, or alternatively that they represent false equilibria arising from recrystallisation or interconversion, the possibility of which we shall consider in due course. We therefore attach no significance to arrests only encountered once. It must be stressed that each of the arrests in series II which have been ascribed to the existence of forms *e*—*j* appeared on not less than three occasions, with the degree of reproducibility given above. It is worth recording that the highest m. p.s tended to be encountered when the solid was heated comparatively rapidly.

In the one run with crystals which had been produced by warming of the glass, the melting behaviour was quite different. The temperature–time curve for this experiment is plotted in Fig. 4. It has several horizontal or almost horizontal portions, which fall in the temperature range covering the m. p.s observed in series I. Whether or not all the arrests represent m. p.s, there is no doubt that in this experiment melting started at about 138·8° K., and that fusion was complete at 142° K., *i.e.*, at a temperature at which, in the other experiments of series II, the alkyl compound was still all solid or only just beginning to liquefy. Some, but not all, of the arrests can be correlated with the m. p.s of series I. We shall defer further discussion of this, however, until all the experimental evidence has been presented.

Series III.—In this apparatus crystallisation sometimes occurred with less supercooling than in the experiments already described. When this happened it was possible to carry out measurements of the freezing as opposed to the melting temperatures. Just before crystallisation started the air was pumped away from the space separating the alkyl compound from the cooling agent (liquid oxygen), and temperature–time readings were taken until stirring became impossible. When, however, the supercooling was greater, with the result that considerable quantities of the substance froze rapidly as soon as crystallisation commenced, the stirrer became embedded, and on subsequent warming of the solid by replacing the liquid-oxygen bath by one of solid carbon dioxide–acetone, the temperature as recorded by the thermocouple almost always passed the m. p. by several degrees before the stirrer became free. With the resumption of stirring the temperature fell to the m. p., but shortly afterwards started to rise

FIG. 4.

Temperature–time curve for tetraethyltin (series II), showing the existence of forms of lower melting point than those revealed in Fig. 2. The lower vertical arrow indicates the stage at which the first signs of melting were observed, the upper that at which fusion was seen to be complete.

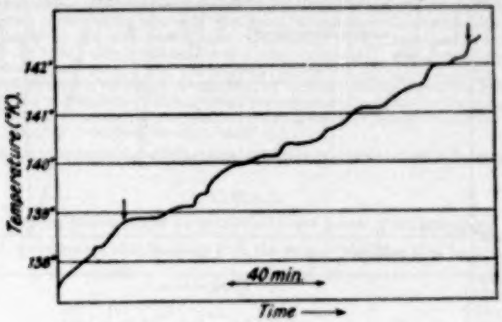
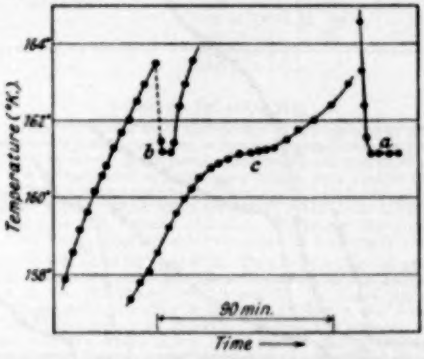


FIG. 5.

Temperature–time curves for carbon disulphide, the apparatus being that of Series III.



again. Since the apparatus was suitable only for observations on the first stages of freezing and the final stages of melting, it was modified after a number of experiments of this kind had been carried out. The stirrer was removed and replaced by a pile of 30 perforated copper discs, 0·1 mm. thick, soldered at a distance of 2 mm. apart to a central metal tube which closely fitted the thermocouple tube. The height of the pile of discs was such that the top disc was just below the surface of the liquid alkyl compound. With this arrangement it was possible to measure the temperature at which fusion of the crystalline mass started, but not the temperatures at which any higher-melting forms present may have begun to liquefy. Experiments were carried out on a pure sample of carbon disulphide, as representing a substance with a single and accurately known m. p., to ensure that with such a substance the melting and the freezing temperature measured in these different ways were in fact identical. In Fig. 5 are shown temperature–time curves for carbon disulphide obtained (*a*) by slow freezing with continuous

stirring, (*b*) by warming the completely crystallised sample, the stirrer being started as soon as it became free, and (*c*) by warming the completely crystallised sample by the copper discs. It will be seen that the value to which the temperature falls in (*b*) as soon as the stirrer operates, and the temperature at which the warming curve (*c*) shows a horizontal point of inflexion are in fact the same as the steady temperature recorded during freezing in (*a*).

FIG. 6.

Temperature–time curves for fusion of tetraethyltin (series III).

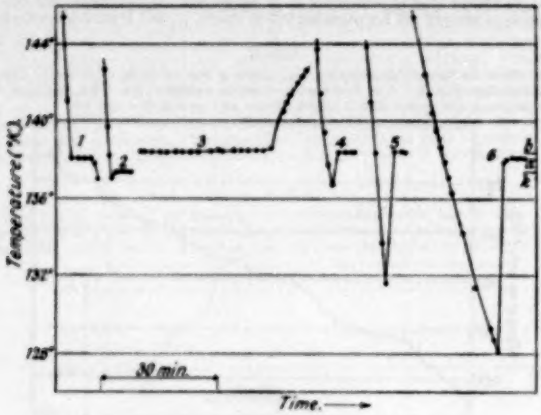
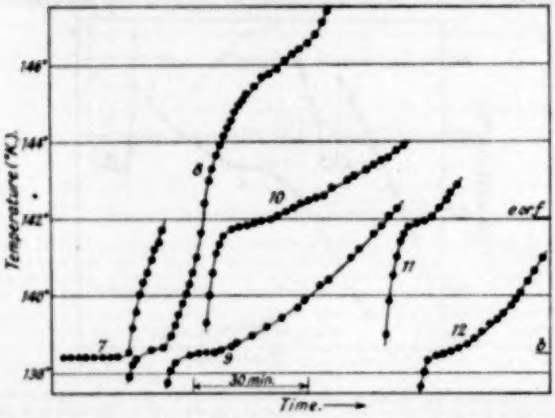


FIG. 7.

Temperature–time curves for fusion of tetraethyltin (series III).



When the alkyl compound was cooled sufficiently rapidly, crystallisation frequently occurred without extensive supercooling, and this always produced the forms with the lowest m. p.s. Slow cooling, however, usually gave the glass, which was then induced to crystallise by gradually raising its temperature.

A representative selection of the temperature–time curves obtained in series III is shown in Figs. 6 and 7. Curve 1 is an example of an experiment in which freezing occurred with scarcely any supercooling, and the corresponding freezing temperature of 138·11° K. suggests that the substance had crystallised in form *a*, twice obtained in series I. The same form was obtained in a later experiment (curve 6) in

which its appearance was preceded by extensive supercooling. Curves 2 and 3 are of particular interest: the arrest in the freezing curve 2 took place at 137·43° K. and must be ascribed to the production of a new form *h* which has the lowest m. p. we have measured for tetraethyltin. As soon as the movement of the stirrer became sluggish the alkyl compound was allowed to warm, and, with the stirrer operating continuously, the warming curve 2 was obtained. There is an arrest in the warming curve which corresponds to m. p. 138·5° ± 0·05° K., *i.e.*, close to the value ascribed to form *b* of series I. The freezing and melting temperatures for curves 2 and 3 are definitely different, and it would seem that in the interval between the cessation of the measurements made during freezing and the start of those made during melting the very low-melting form *h* first produced had spontaneously changed into *b*. Furthermore, the form *b* was frequently produced directly on cooling (curves 4 and 5). In all, form *b* was produced 10 times in series III, its f. p. being obtained in 5 cooling curves, and concordant values for the m. p. in 5 other experiments which are represented in Figs. 6 and 7 (curves 3, 7, 8, 9, and 12).

In 7 of the experiments in which the crystalline alkyl compound was warmed by using the copper-disc technique, the temperature–time curve showed a horizontal or almost horizontal point of indexion at 141·9° ± 0·1° K. This is illustrated by curves 10 and 11 of Fig. 7. This presumably represents the melting of form *e* or *f*, which were frequently produced in series I and II. Finally, in one experiment carried out on crystals obtained by warming the glass, the temperature when the stirrer ultimately became free fell to 145·8° K. and remained at this temperature for 4 minutes before rising again. This agrees with the m. p. of form *i* which was obtained 6 times in series II. Very possibly some of the alkyl compound was present in this form in the experiment represented by curve 8 of Fig. 7. The course of this curve in the neighbourhood of 146° K. suggests that further melting was taking place in this region. In this case the copper-disc technique was employed and an accurate value for the higher m. p. cannot be given, but at least it seems clear that the crystalline alkyl compound was partly in the form *b* and partly in a form with a m. p. higher than that of *e* or *f* (~142° K.).

The results of the three independent series of experiments are summarised in Table I.

TABLE I.

Melting points of the various crystalline forms of tetraethyltin.

(The number in parentheses after each m. p. is the number of times that form was obtained.)

Form.	Series I.	Series II.	Series III.
h	—	—	137·43° (2)
a	138·1° ± 0·1° (2)	—	138·11 (2)
b	138·7 ± 0·2 (5)	—	138·5 (10)
c	139·8 ± 0·05 (6)	—	—
d	140·61 (4)	—	—
f	141·87 (7)	—	141·9 ± 0·1 (7)
e	142·12 (5)	142·1° ± 0·1° (5, ?7)	—
g	—	143·15 ± 0·05 (3, ?4)	—
k	—	144·1 ± 0·15 (1, ?3)	—
i	—	145·8 ± 0·1 (6)	145·8 (1, ?2)
j	—	147·1 ± 0·15 (5)	—

Results for Tetraethyl-lead.

All the experiments on this substance were carried out in the apparatus used for series III of the tetraethyltin work. It was never possible to make temperature measurements during freezing. Crystallisation could only be induced by warming the supercooled substance, and started at least 10° below the lowest m. p. recorded. The formation of crystals, once begun, was usually so rapid that the stirrer became frozen in, although in 2 experiments (curves 2 and 4 of Fig. 8) it was possible to keep the stirrer just in motion throughout. Consequently all observations were made during melting, either with mechanical stirring (as soon as this became possible), or else by the copper-disc technique. A representative selection of the temperature–time curves obtained is shown in Fig. 8.

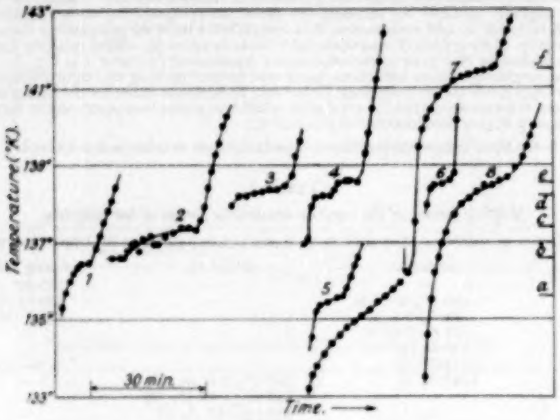
The lowest m. p. observed was at 135·6° ± 0·1° K. This form *a* was obtained in 3 of a total of 13 experiments. The results of one of these are shown in curve 5. A second form *b* with m. p. 136·6° ± 0·1° K. appeared on two occasions (curves 1 and 2). In the second of these, stirring never completely ceased, and the temperature, after remaining at 136·6° K. for 4 minutes, then rose very irregularly before again becoming constant at 137·4° K. Evidence of a form *c* with m. p. 137·4° K. was furnished by 2 other runs, and accordingly it is possible that, in the experiment which gave curve 2, some of the liquid produced from form *b* crystallised again as *c*, and that during the two arrests the system was not in equilibrium, the temperature oscillation being due to the opposing thermal effects associated with the crystallisation of *c* and the fusion of the remaining *b*.

Curve 4 indicates the melting of two forms *d* and *e* with m. p. 138·2° and 138·55° K. respectively. The modification *d* also seemed to have been produced in the experiment represented in curve 3, perhaps again accompanied by a small amount of *e*, but crystallisation as *e* was altogether more common. In all it appeared to be present on 8 occasions. Lastly, curve 7 provides evidence for the existence of a form *f* with a much higher m. p. (141·5° K.). The lower part of this curve, the measurements for which were made while the stirrer was still immovable, suggests the presence of a low-melting modification, probably *a*. As soon as the stirrer was started (at the point shown by the gap in the curve) the temperature rose extremely rapidly, suggesting that crystals were once more being formed, and then followed the course shown.

Since the experiments of series III on tetraethyltin revealed the existence of only about half of the modifications found altogether, the polymorphism of tetraethyl-lead may not be limited to the 6 forms just described, and in particular there may be other modifications of higher rather than lower m. p. The question arises whether any correlation exists between the m. p.s of the different forms of the two alkyl compounds, and it is interesting that it is possible to associate 5 of the alkyl-lead forms with 5 of the tetraethyltin modifications, so that the differences in m. p. between the members of each pair are almost constant. The pairs are as follows (the first letter of each pair refers to the alkyl tin, and the figures give the amount by which the m. p. of the tin exceeds that of the lead compound): *b–f*, 2·6°; *d–d*, 2·4°, *e–e*, 2·4°; *b–b*, 2·1°; *a–a*, 2·5°. This parallelism may, however, be fortuitous, as the m. p.s of the several forms of any one substance are so close together. Almost equally constant m. p. differences (of ~5·5°) in fact are found for the pairs *f–f*, *b–e*, *g–c*, *e–* or *f–b*, *d–a*.

FIG. 8.

Temperature–time curves for the fusion of crystalline tetraethyl-lead. In the experiment represented by curve 7, the stirrer came into operation at the gap in the curve indicated by the arrow.



Experiments on Tetraethylgermanium.

Dennis and Hance (*J. Amer. Chem. Soc.*, 1925, **47**, 370) gave 183·0° K. as the m. p. of this substance. We have carried out preliminary experiments on a sample (specially prepared for us by the method described by Krause and Flood, *ibid.*, 1932, **54**, 1635), which unfortunately proved to be much less pure than was hoped. Eight experiments were carried out in the apparatus used for the tetraethyltin investigations. Crystallisation could be brought about by rapid cooling, with little if any supercooling. With slower cooling, the alkyl compound could be supercooled by about 15°. The 6 cooling and 3 warming curves obtained gave no indication that the substance had ever crystallised in any but one form, and, though an accurate value for the m. p. of this cannot at present be given, it is certainly within 1—2° of the value found by Dennis and Hance.

DISCUSSION.

As far as we are aware, no other known organic substance is capable of existing at ordinary pressures in as many crystalline forms as tetraethyltin. In the comprehensive investigation of the physical properties of hydrocarbons carried out at the National Bureau of Standards, Washington, a few of these substances have been found to crystallise in three different forms, *e.g.*, **3**:3-dimethylpentane and mesitylene (Streiff, Murphy, Sedlak, Willingham, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 331), and menthol can exist in at least four solid modifications with melting points only a few degrees apart (Wright, *J. Amer. Chem. Soc.*, 1917, **39**, 1515). For tetraethyltin, however, there appear to be at least ten forms, and for tetraethyl-lead at least six. The only value in the literature for the melting point of tetraethyltin is 161° K., quoted by Grüttner and Krause (*Ber.*, 1917, **50**, 1802), who do not, however, give any details about its determination. This value is considerably higher than any we have obtained.

One striking feature of our experiments has been the frequency with which crystallisation has produced more than one modification simultaneously, as shown from the resulting step-wise melting curves. In these circumstances the system during melting cannot really be in

equilibrium, and the fact that the melting curves so often resemble those which would be obtained by heating a mixture of substances which melt to quite immiscible liquids implies that, with the higher-melting forms at least, the velocity of crystallisation of any given form from the liquid at temperatures a little below the melting point is small in relation to the time of a melting experiment. In fact, in only one experiment did it definitely appear that the melting of a low-melting form was followed by rapid recrystallisation to a modification of higher melting point (see curve 7 in Fig. 8). The spontaneous change of one solid modification into another also appeared to be comparatively rare, although this definitely happened once with tetraethyltin in series III (curves 2 and 3 of Fig. 6) and probably also in series II, since when steady temperatures were recorded during freezing they were lower than those at which the crystal melted. It is also possible that either recrystallisation from the liquid or spontaneous change of one form into another, or both of the effects simultaneously, may have been responsible for the unusual temperature–time curve shown in Fig. 4. The combination of the thermal changes caused by these effects with those caused by melting of the crystals could produce chance arrests and changes of slope in the melting curve and may explain why not all the arrests in Fig. 4 can be correlated with the melting points observed in this region in series I or III. It is worth pointing out that the velocity with which a liquid freezes is sometimes very sensitive to the presence of traces of impurities (Timmermans, " Chemical Species," Macmillan, 1941, p. 103), and that the same may be true of the velocity of spontaneous change of one solid form of a substance into another. Consequently, effects due to recrystallisation and to interconversion of the crystal forms might be obtained with one sample of the alkyl compound but not with another which differs slightly in the amount and nature of the impurities present.

In seeking an explanation of the unusual polymorphism of tetraethyl-tin and -lead, we attach considerable importance to differences between these substances and certain analogues : calorimetric studies in this laboratory on tetramethyl-tin and -lead, tetraethylgermanium, and 3 : 3-diethyl-*n*-pentane have given no indication of multiple melting points. Aston and Messerly (*J. Amer. Chem. Soc.*, 1936, **58**, 2354) reported only one melting point for *neo*pentane, although tetramethylsilicon crystallised in a stable and an unstable modification (Aston, Kennedy, and Messerly, *ibid.*, 1941, **73**, 2343). Among the Group-IV tetramethyl and tetraethyl compounds, therefore, tetraethyl-tin and -lead appear to be in a class by themselves with respect to their polymorphism. But there is a further important difference between the tetraethyl and tetramethyl compounds, concerned with the trend of the melting points on progression from carbon to lead. Table II records the melting points of these substances and of the tetrachlorides. Both for the tetramethyl compounds and for the tetrachlorides the melting point of the carbon

TABLE II.

Melting points (K.) *of compounds* MX_4.

M.	Cl.	CH_3.	C_2H_5.	M.	Cl.	CH_3.	C_2H_5.
C	250·3°	256·5°	240·1°	Sn	240°	218·3°	147·1° *
Si	203·3	174·1	—	Pb	238	242·9	141·8 *
Ge	224	185	183·0				

* Highest melting point recorded.

compound is higher than that of the silicon compound. Thereafter the melting point rises with increasing molecular weight. The same is true for the bromides and iodides. The relatively high melting points of the carbon compounds are to be related to the fact that they all [*i.e.*, $C(CH_3)_4$, CCl_4, CBr_4, and CI_4] exist in a low-temperature and a high-temperature form. For CBr_4 and probably for the other tetra-halides the high-temperature form has a highly symmetrical lattice. The short C–X bond length leads to a compact and nearly spherical CX_4 molecule and a lattice of considerable symmetry such that the molecules, even if they do not freely rotate, probably have considerable orientational freedom and behave as if they were effectively spherical. The greater Si–X bond length and the stronger intermolecular forces lead to a greater degree of intermolecular interlocking, and a lattice which, while perhaps isomorphous with the low-temperature form of CX_4, is certainly not isomorphous with the high-temperature form. Consequently, the melting-points of the CX_4 compounds do not fall into line with those of the corresponding compounds of the later elements of the group. It may be remarked here that " tetraethylcarbon " (3 : 3-diethyl-*n*-pentane) has been found in this laboratory to undergo a transition some 30° below its melting point, which, as will be seen from Table II, is higher than that of the other known Group-IV tetraethyl derivatives.

The tetraethyl have lower melting points than the corresponding tetramethyl compounds,

and there is no longer an upward trend from germanium to lead. The highest melting point of tetraethyltin is considerably lower than that of tetraethylgermanium. This suggests that, while for the tetramethyl compounds or a set of halides, the solids from silicon to lead are isomorphous, this is no longer true for the tetraethyl compounds, and that the change from germanium to tin means a departure from the crystalline form of solid $Ge(C_2H_5)_4$ and the introduction of remarkable possibilities of polymorphism.

Probably the most important change in the MX_4 molecules (X = alkyl) in the progression from M = C to M = Pb is the M–X bond length, *viz.*, C–C 1·54, Si–C 1·93, Ge–C 1·98, Sn–C 2·18, and Pb–C 2·29 A. (Brockway and Jenkins, *ibid.*, 1936, **58**, 2036). The most marked changes in bond length are associated with the stages C→Si and Ge→Sn. We have already considered the effect of the first of these. The second is believed to be intimately connected with the polymorphism of tetraethyl-tin and -lead.

There is reason to believe that the potential barrier restricting the rotation of a methyl group about the bond joining it to an atom decreases rapidly as this bond length increases, and that whereas in $C(CH_3)_4$ this barrier height is 5000 kcals., in $Si(CH_3)_4$ it is only 1300 kcals. (Aston, Kennedy, and Messerly, *loc. cit.*), and in $Sn(CH_3)_4$ and $Pb(CH_3)_4$ it is probably almost nil (French and Rasmussen, *J. Chem. Physics*, 1946, **14**, 389). However, even if the methyl groups in compounds $M(CH_3)_4$ rotate freely, the ethyl groups in $M(C_2H_5)_4$ cannot do so owing to the overlap of the paths followed by the peripheral atoms. Fig. 9 shows, for $C(C_2H_5)_4$, $Ge(C_2H_5)_4$, and $Pb(C_2H_5)_4$, the position in which this overlap is greatest. The radii of the full circles are in proportion to the covalent radii of the atoms concerned. The dotted circles represent the effective van der Waals field of action of the peripheral methyl groups, the radius corresponding to 2 A. (Stuart, "Molekülstruktur," Berlin, 1934, p. 47). It will be seen that even with the largest molecule (tetraethyl-lead) there is a considerable overlap of the regions swept out by the van der Waals' spheres of action of the methyl groups as the ethyl groups rotate. In an isolated molecule it will, of course, be possible for any one methyl group to proceed to any other position which free rotation about the M–C bond makes available to it, though this may require simultaneous and suitable movement on the part of the other methyl groups. (The potential energy of a pair of methyl groups could be approximately represented by an expression such as $[(a/r^{12}) - (b/r^6)]$, where r is the separation of their centres. It would be interesting to know if the total potential energy of all four such groups in a molecule, expressed in terms of co-ordinates defining their relative positions, has more than one minimum. Unfortunately, the mathematical difficulties involved in the solution of this problem appear considerable.)

FIG. 9.

Showing the relationship of two co-planar ethyl groups in tetraethyl-germanium and -lead and 3 : 3-diethyl-n-pentane.

The freedom of movement of the methyl groups of any one tetraethyl molecule will, however, be further restricted in the condensed states if under these conditions adjacent molecules tend to interlock. Nothing is known of the crystal structure of the solids. However, calculations from the van der Waals spheres of action of the methyl groups and the molar volumes show that there must be considerable intermolecular interlocking *in the liquid*, and presumably even more in the solid. This will be more pronounced the larger is the central atom. By means of models, it can be shown that for a tetraethyl molecule with a sufficiently large central atom, various forms can be constructed, differing in the relative positions of the methyl groups, such that the molecules of any one form can be packed together so as to prevent the methyl groups altering their positions to those of another form.

The polymorphism of tetraethyl-tin and -lead may not therefore be simply caused by packing of identical molecules into a suprisingly large number of different lattices, but rather by the molecular geometry and dimensions being such that different crystal forms exist in which the

relationship between the methyl groups in one molecule, and hence between those in adjacent molecules, is different from one form to another. (There may, of course, be polymorphism of the ordinary kind as well, in that some of the crystalline forms may contain molecules with identical configurations.) In other words it is suggested that, in the crystalline solids at least, these molecules exhibit a form of rotational isomerism. In the smaller molecules of the carbon and germanium series there is a larger potential barrier restricting free rotation of the ethyl groups about the bonds to the central atom, as well as greater overlap of the regions available to the peripheral groups and less pronounced intermolecular interpenetration (*i.e.*, the molecules are more compact and more nearly spherical). These factors may combine to make one configuration of the molecule in the lattice much the most stable.

If rotational isomers of tetraethyl-tin and -lead exist in the solid, the question of their possible persistence in the liquid state arises. For example, is the liquid produced as a high-melting form melts identical with that obtained by heating to the same temperature the liquid produced from a low-melting modification. If intermolecular equilibrium in the liquid is very rapidly established at all temperatures, so that the free energy of the liquid (at constant pressure) has a definite value at a given temperature (whatever the history of the liquid), then we should expect constant and reproducible melting points for the different solid forms of the pure substance (in the absence of complications such as spontaneous recrystallisation or interconversion). Comparatively slow attainment of the equilibrium in the liquid would lead to a time-variable free-energy curve and variable freezing and melting points (*i.e.*, the melting point of a given form should change as melting proceeds; the properties of systems such as this would be have been fully discussed by Smits, in "The Theory of Allotropy," Longmans, 1922.) Our results appear to conform to the first type of behaviour, and suggest that, in the neighbourhood of the melting points at least, any equilibrium in the liquid is established relatively rapidly. This does not, however, rule out the possibility that the liquid shows time-variability in its properties, particularly at lower temperatures in the supercooled state, and it is hoped to investigate this further. Claims to have observed hysteresis in the thermodynamic properties of organic liquids are of doubtful reliability (see Aston and Schumann, *J. Amer. Chem. Soc.*, **1942**, **64**, 1034; Guthrie and Huffman, *ibid.*, **1943**, **65**, 1143; Aston, Rank, Sheppard, and Szasz, *ibid.*, **1948**, **70**, 3525; Railing, *ibid.*, **1939**, **61**, 3349; and Pitzer, *ibid.*, **1940**, **62**, 331).

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471. *The Nature of the Co-ordinate Link. Part I. The Non-ionic Complex Compounds of Tri-n-propylphosphine with Platinic and Platinous Chlorides.*

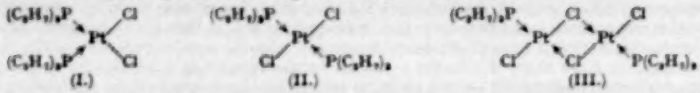
By J. CHATT.

The non-ionic simple complexes *cis*-$[(C_3H_7)_3P]_2PtCl_2$ (I), *trans*-$[(C_3H_7)_3P]_2PtCl_2$ (II), and the bridged complex $[(C_3H_7)_3P,PtCl_2]_2$ (III) have been oxidised to the corresponding platinic complexes (IV), (V), and (VI), which have all been characterised.

Chlorination of the simple complexes is easy and clean but that of the bridged complex does not go cleanly. The *cis*-platinic complex (IV) is much more labile than its platinous analogue and isomerises in benzene solution, slowly at room temperature, rapidly on boiling. Thermal decomposition of both the *cis*- and *trans*-platinic complexes yields a mixture of *cis*- and *trans*-platinous complexes from each isomer, indicating a *cis*-elimination of the chlorine atoms. The simple platinic complexes are surprisingly resistant to reduction by sulphur dioxide but each yields a mixture of the *cis*- and *trans*-platinous complexes by stannous chloride reduction. The bridged platinic complex (III) is on the other hand easily reduced. Its properties contrast with those of the bridged platinous complex in that the bridge is very weak and is split by ether and other oxygen-containing solvents, rather like the bridge in aluminium chloride. The platinic bridged complex also shows catalytic activity not shown by any other of these six complexes. It is suggested that the *d* orbitals of the platinum atom take part in a resonance which stabilises the platinous bridge but is less likely to take place in a platinic bridge because another *d* orbital is now involved in principal valency formation. Tri-*n*-propylhydroxyphosphonium chloroplatinate, chloroplatinite, and tetrachloro-*pp*′-dichlorodiplatinite are described.

HITHERTO only two series of complex compounds of tertiary phosphines with platinum chlorides have been described. In the n-propyl series they are *cis*- and *trans*-bis(tri-*n*-propyl-

phosphine)dichloroplatinum (I and II). Their configurations have been determined by dipole-moment measurements (Jensen, *Z. anorg. Chem.*, 1936, **229**, 250).



The third platinous complex, dichlorobis(tri-*n*-propylphosphine)-$\mu\mu'$-dichlorodiplatinum (III), was first obtained by reaction of the phosphine with ethyleneplatinous chloride $(C_2H_4PtCl_2)_2$ but is more conveniently prepared by the direct reaction at about 165° of finely powdered platinous chloride with the crude mixture of (I) and (II) prepared by Jensen's method. This compound is a platinum analogue of the palladium compounds described by Mann (*Ann. Reports*, 1938, **35**, 150; Chatt and Mann, *J.*, 1939, 1622), but could not be obtained by the method available in the palladium series (Mann and Purdie, *J.*, 1936, 880).

The properties of this class of compound will not be described here; other members have been prepared and isomerism in this series is at present under investigation.

It has been observed (Nyholm, *Quart. Reviews*, 1949, **3**, 343) that the most stable halogen-bridged complex compounds are those in which the metal, which is usually multivalent, exists in one of its lower valency states. In view of the ready and clean halogenation of the simple complex compounds of tertiary arsines with platinous halides to the corresponding platinic compounds (Nyholm, *J.*, 1950, 843), it was of interest to see whether the bridged platinous complex compounds were so easily and cleanly oxidised and whether the halogen bridge would survive such treatment.

Chlorination of the bridged complex (III) was, however, far from clean; some propylphosphine was oxidised away from the platinum atom, and the properties of the derived platinic complex (VI) were very different from those of the platinous bridged complex (III). On the basis of the formulæ as written, (I), (II), and (III), there is no obvious reason why (III) should behave so differently on chlorination; consequently, the oxidation of these three substances was of immediate interest for the light it might throw on the detailed structure of the halogen bridge.

Chlorination of the Platinous Complexes (I), (II), and (III).—When the simple compounds (I) and (II) were treated in benzene solution at 0—5° with the theoretical quantity of chlorine in carbon tetrachloride solution, the oxidation proceeded smoothly and cleanly. The crystalline platinic derivatives crystallised from the reaction mixture as Nyholm described for the simple arsine complexes (*J.*, *loc. cit.*). There was only very slight chlorination of the benzene, as shown by a slight fume of hydrogen chloride. Some isomerisation of the *cis*-compound (IV) also occurred during the chlorination:

$$cis\text{-}(PPr_3)_2PtCl_2 + Cl_2 = 70\%\ cis\text{-}(PPr_3)_2PtCl_4 + 30\%\ trans\text{-}(PPr_3)_2PtCl_4$$
$$trans\text{-}(PPr_3)_2PtCl_2 + Cl_2 = trans\text{-}(PPr_3)_2PtCl_4$$

These chlorinations can be effected most conveniently by passing an excess of chlorine into the benzene solutions, then immediately filtering off the *cis*-product or removing the excess of chlorine by partial evaporation under 15 mm. pressure in the preparation of the *trans*-isomer.

The products *cis*- and *trans*-bis(tri-*n*-propylphosphine)tetrachloroplatinum (IV) and (V) are beautifully crystalline substances less soluble in benzene and more strongly coloured than their progenitors. Unlike the simple platinic derivatives of tertiary arsines studied by Nyholm (*J.*, *loc. cit.*) they both decompose on melting. The *cis*-isomer melts at 123—125°, immediately resolidifies, and remelts over a long range at 175—200°. The *trans*-isomer melts at 175—185° depending on the rate of heating.

The *cis*-configuration was assigned to the greenish-yellow isomer, and the *trans*-configuration to the golden-yellow isomer, on the basis of the following contrasting properties:

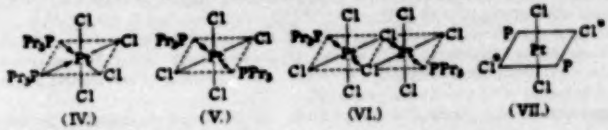
cis-$(PPr_3)_2PtCl_4$.	*trans*-$(PPr_3)_2PtCl_4$.
Obtained only by chlorination of *cis*-$(PPr_3)_2PtCl_2$.	Obtained as the only product in the chlorination of *trans*-$(PPr_3)_2PtCl_2$.
Insoluble in cold benzene and non-polar solvents.	Fairly soluble in cold benzene and most organic solvents.
Labile, converted into its isomer in boiling solvents.	Not labile; no physical conditions caused isomerisation.
Develops a cloudiness with silver nitrate in aqueous acetone.	Stable to silver nitrate.

The chlorination of the bridged complex (III) was in marked contrast. In benzene solution considerable chlorination of the benzene occurred even when the theoretical quantity of chlorine

was used. A deliquescent yellow oil separated. The benzene solution decanted from the oil yielded ultimately only a very small quantity of hexachlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum, (VI), together with a little unchanged (III). When an excess of chlorine was used, very rapid chlorination of the benzene occurred and the oil was the only product.

The preparation of (VI) was therefore carried out in chloroform solution by using the theoretical quantity of chlorine. Even then only a yield of about 30% was obtained, together with gummy and oily by-products and a small quantity of the salt, $[PPr_3{\cdot}OH]_2[Pt_2Cl_6]$. This must be a secondary hydrolysis product derived from tri-*n*-propylphosphine dichloride, indicating that in this chlorination some of the phosphine is oxidised away from the metal atom.

Hexachlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum (VI) is either insoluble, or decomposes, in all organic solvents tried, so neither its complexity nor its configuration could be established. To retain the octahedral configuration of groups round the platinum atoms the dimeric formula $(PPr_3PtCl_4)_2$ was assumed. The existence of a halogen bridge in the molecule is supported by the orange colour in contrast to the yellow colours of the simple platinic derivatives. The *trans*-configuration is probable because the simple platinic derivatives were found to be much more labile than their platinous analogues and the halogen bridged platinous derivatives are so labile that only the *trans*-symmetrical forms have so far been isolated.



(IV.) (V.) (VI.) (VII.)

The following four comparative studies of the above six complex compounds have been made:

(1) *Isomerisation of* (IV) *into* (V), (I) *into* (II), *and* (II) *into* (I).—The co-ordinating groups in the *cis*-platinic complex (IV) show a very much greater lability than in the corresponding platinous complex (I). In boiling benzene isomerisation occurs rapidly, and even at room temperature a suspension of (IV) in benzene showed 25% isomerisation in 5 days. In boiling acetone 20% isomerisation was found after 1 hour and none of the *cis*-isomer remained after 15 hours.

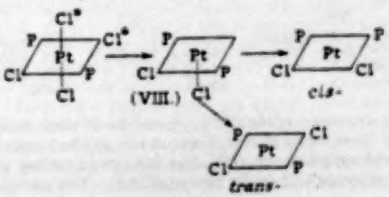
In contrast *cis*-$(PPr_3)_2PtCl_2$ (I) was isomerised only to the extent of 55% after being held in a molten condition for 2½ hours at 160° and 88% at 195°. The reverse change occurred in the same time to the extent of 6·5% at 160° and 3·5% at 195°. No isomerisation of the *cis*-isomer occurred during 15 hours' boiling of its acetone solution.

(2) *Thermal Decomposition of* cis- *and* trans-$(PPr_3)_2PtCl_2$ (IV and V).—The thermal decomposition of the *trans*-platinic complex (V) provided an example of the production of a *cis*-isomer by the thermal decomposition of a compound of *trans*-configuration:

$$trans\text{-}(PPr_3)_2PtCl_2 \xrightarrow[\text{for 15 mins.}]{\text{heat at 195°}} 9\%\ cis\text{-} + 14\%\ trans\text{-}(PPr_3)_2PtCl_2 + 77\%\ \text{black oily substances}$$

This transformation can be explained only on the basis of a *cis*-elimination of the chlorine atoms. If a *trans*-elimination occurred, *i.e.*, the removal of the starred atoms in (VII), it would lead at once without any rearrangement of the molecule to *trans*-$(PPr_3)_2PtCl_2$. In this event the quantity of *cis*-material in the product could not exceed the equilibrium concentration (~4%) and would most probably be of the order of ½% because equilibrium is only very slowly established.

A *cis*-elimination on the other hand leaves an intermediate (VIII) in which the groups are not in a planar configuration, and during the subsequent rearrangement either a *cis*- or a *trans*-configuration could be assumed by the molecule:—



It was also found that stannous chloride reduction of *trans*-$(PPr_3)_2PtCl_4$ produced a mixture of *cis*- and *trans*-$(PPr_3)_2PtCl_2$, so it may be that a *cis*-elimination rule is applicable to these platinic complexes as the classical *trans*-elimination rule is to the platinous ammines (Werner, *Z. anorg. Chem.*, 1893, **3**, 267).

The thermal decomposition of *cis*-$(PPr_3)_2PtCl_4$ (IV) also produced a similar mixture of *cis*- and *trans*-$(PPr_3)_2PtCl_2$. The decomposition occurred at 135—140°, a lower temperature than was possible with the *trans*-isomer, and the product was free from black and oily by-products. The decomposition occurred as follows:

$$3\ cis\text{-}(PPr_3)_2PtCl_4 = 2(PPr_3)_2PtCl_2 + [PPr_3Cl]_2[PtCl_4]$$
(IX.)

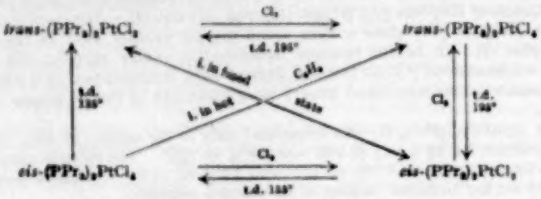
The salt (IX) was isolated as it hydrolysis product tri-*n*-propylhydroxyphosphonium chloroplatinate, $[PPr_3{\cdot}OH]_2[PtCl_4].2H_2O$, also obtained by direct synthesis by the following series of reactions:

$$PPr_3 + Cl_2 = PPr_3Cl_2;\ 2PPr_3Cl_2 + H_2PtCl_4 = [PPr_3Cl]_2[PtCl_4] + 2HCl;$$
$$[PPr_3Cl]_2[PtCl_4] + 4H_2O = [PPr_3{\cdot}OH]_2[PtCl_4].2H_2O + 2HCl$$

This salt was also characterised as its anhydrous chloroplatinite $[PPr_3{\cdot}OH]_2[PtCl_4]$ and its tetrachloro-μμ′-dichlorodiplatinite $[PPr_3{\cdot}OH]_2[Pt_2Cl_6]$ obtained during chlorination of (III).

That the decomposition of *cis*-$(PPr_3)_2PtCl_4$ occurs at a lower temperature and more cleanly than its *trans*-isomer indicates that isomerisation does not occur before decomposition. Isomerisation does occur simultaneously, however, and 40—50% of the *trans*-platinic complex was isolated together with the above products.

The isomerisation and thermal decomposition reactions are summarised in the following diagram:



(i. = Isomerisation. t.d. = Thermal decomposition.)

(3) *Reduction of the Platinic Complexes* (IV), (V), *and* (VI) *to the Corresponding Platinous Compounds.*—The simple platinic complexes showed unexpected resistance to reduction. The *cis*-isomer was rather more easily reduced than the *trans*-isomer and stannous chloride was the only satisfactory reducing agent used. A mixture of *cis*- and *trans*-$(PPr_3)_2PtCl_2$ was produced in each case. The product obtained from the *cis*-platinic complex contained 64%, and that from the *trans*-platinic complex 15%, of the *cis*-platinous complex.

By way of contrast the bridged platinic complex (VI) showed a marked tendency to revert to the platinous state. Even if it was allowed to remain in a sticky condition damped with acetone or some similar solvent the bridged platinous complex (III) would start to crystallise from the gum after a few days.

Under comparable conditions reduction by various reducing agents occurred as below. The sulphur dioxide (20% excess) and the stannous chloride reductions were carried out in aqueous acetone.

Reducing agent.	(IV.)	(V.)	(VI.)
KI	I_2 very slowly liberated	No free I_2	I_2 liberated comparatively rapidly
Boiling acetone ...	5—10% Redn. (14 hrs.)	No redn. (14 hrs.)	25% Redn. (4 hrs.)
SO_2 (5 days)	15% Redn.	<5% Redn.	30% Redn.
$SnCl_2$	Redn.	Redn.	Redn.

(4) *Comparison of the Properties of the Platinous and the Platinic Bridged Complexes* (III) *and* (VI).—The properties of these bridged complexes are in marked contrast. Dichlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum (III), like the corresponding palladium compounds, is easily soluble in organic solvents and easily recrystallised. The platinic bridged complex (VI)

is only sparingly soluble in all the organic solvents tried, with the exception of acetone and similar substances which split the bridge. It could not be recrystallised.

The bridge in the platinic complex (VI) is very much weaker than in the platinous complex (III). The former is readily split by oxygen-containing solvents such as esters, alcohol, acetone, and ether. Thus a solution in ether on evaporation under reduced pressure produces the very beautifully crystalline, yellow etherate which is extremely soluble in ether. It loses ether on exposure to the air, or more rapidly in a vacuum, thus reverting to the orange bridged complex (VI):

$$\text{(VI.)}\quad (PPr_3PtCl_4)_2 + 2Et_2O \rightleftharpoons 2Et_2O,PPr_3PtCl_4$$

This reaction was used for the isolation and purification of (VI). A similar substance (not analysed) was obtained from acetone solution. It follows that all the reactions of the platinic bridged complex taking place in solution are really the reactions of such substances as the above etherate and acetonate.

Etherates in the platinous series are unknown and the platinous bridge is not split by ether; it is, however, split by the more strongly co-ordinating molecule, *p*-toluidine, in the same manner as the corresponding palladium compounds (Mann and Purdie, *J.*, 1936, 876):

$$(PPr_3PtCl_2)_2 + 2CH_3{\cdot}C_6H_4{\cdot}NH_2 = 2PPr_3CH_3{\cdot}C_6H_4{\cdot}NH_2PtCl_3 \quad \text{(X.)}$$

The platinic bridged complex gives a similar product in ether solution:

$$PPr_3Et_2O,PtCl_4 + CH_3{\cdot}C_6H_4{\cdot}NH_2 = \underset{\text{(XI.)}}{PPr_3CH_3{\cdot}C_6H_4{\cdot}NH_2PtCl_4} + Et_2O$$

(XI) has a so been obtained by direct chlorination of (X).

The platinic bridge is split by concentrated hydrochloric acid, in which the compound (VI) dissolves in about an hour to give a yellow solution. The product or products were not identified. The bridged platinous complex is not affected after being in contact with the acid for a few days, but dissolves gradually during a few months.

The bridged platinic complex (VI) is also a powerful catalyst for the polymerisation of acetaldehyde, further emphasising its electron-seeking character. Neither the bridged platinous complex (III) nor the simple platinic complexes (IV and V) react in this manner. The bridged platinic complex also acts as a catalyst in the chlorination of benzene.

This work has raised two interesting points: (1) In the bridged series of complexes the platinous state has a much greater stability relative to the platinic state than it has in the simple complexes. (2) The bridge in the platinic bridged complex, if it exists, is so weak that it shows considerable resemblance to the bridge in aluminium chloride and this resemblance is extended to the catalytic activity of bridged platinic complexes.

The difference in behaviour between the simple and bridged complexes towards chlorination receives no explanation on the basis of formulæ (I), (II), and (III), in which the platinum atoms are in exactly similar states. Neither can the difference be explained on steric grounds, because even if there was not room for four chlorine atoms to add to the molecule (III), two should readily attach themselves to one of the platinum atoms. If we consider the probable dimensions of the molecule it is found that there is room for all four added chlorine atoms with negligible overlap of the van der Waals radii.

We must look to the detailed structure of the platinous bridge itself for an explanation of its stability. It appears to be stabilised in some manner, perhaps by a resonance which is not possible, or possible only to a lesser extent, in the platinic and the aluminium chloride bridges. The usual formulation, as in formula (III), of the halogen bridge is not entirely satisfactory on empirical grounds (Jensen and Asmussen, *Z. anorg. Chem.*, 1944, **252**, 234) and the above work further emphasises its unsatisfactory character, although it produces no support for the type of resonance proposed by Jensen.

The comparative resistance to chlorination, shown by the bridged platinous complex, suggests that the resonance involves filled *d* orbitals on the metal atom, thus reducing their availability for raising the valency state of the metal. When the metal has been oxidised to the platinic state, their availability for resonance in the bridge is reduced, thus reducing the stability of the bridge. The platinic halogen bridge is thus closer to that in aluminium chloride where there are no filled *d* orbitals. Both these halogen rings are split by ether and like substances, and the acceptor properties of the metal promote catalytic activity. Perhaps it is significant that the metals which form the most stable halogen bridged structures, *viz.*, Pd^{II}, Pt^{II}, Au^{III}, and to a lesser extent Zn, Cd, Hg and Cu, are heavy metals at the end of the transition series where the *d* orbitals are on an energy level close to the *s* and *p* levels. Also, most stable halogen bridges

are formed by metals showing square co-ordination, thus having a natural angle of 90° which is just that between *d* orbitals and would favour the formation of dative double bonds (Chatt, *Nature*, 1950, **165**, 637).

Experimental.

Microanalyses: * by Drs. Weiler and Strauss, Oxford; † by Messrs. Weisser and Ritter, Basle; ‡ by Mr. Thomas, I.C.I. Paints Division, Slough; § by Mr. Brown, Butterwick Research Laboratories; ‖ by Dr. Chambers, British Rubber Producers Research Association, Welwyn Garden City.

cis- and trans-*Bis(tri-n-propylphosphine)dichloroplatinum* (I and II).—Jensen (*loc. cit.*) obtained a mixture of these compounds by reaction of tri-n-propylphosphine with aqueous potassium chloroplatinite. The quantity of the *trans*-isomer is variable, rarely greater than 20% and usually less than 10% of the mixture. Consequently, Jensen's method was used to prepare the *cis*-isomer. The *trans*-isomer was prepared by reaction of the phosphine with the bridged platinous complex (III) (0·5 mol.) in chloroform solution. The mixture of isomers thus obtained contained 85% of the *trans*-isomer. The m. p.s of the pure isomers were *cis*-, 150—151°; *trans*-, 85—86°. Jensen records 149—150° and 82—82·5°, respectively.

Dichlorobis(tri-n-propylphosphine)-μμ'-dichlorodiplatinum (III).—A mixture of the dry crude isomeric bis(tri-n-propylphosphine)-dichloroplatinums (11·45 g.) prepared by Jensen's method and finely powdered platinous chloride (5·5 g., 5% excess) was heated with stirring to 165° for 15 minutes, the melt becoming pasty. The product, when cold, was dissolved in hot acetone, boiled with a very little charcoal, filtered, and evaporated to crystallisation. Almost pure *dichlorobis(tri-n-propylphosphine)-μμ'-dichlorodiplatinum* (III), 12·5 g., m. p. 180—182°, separated in beautiful yellowish-orange needles. Recrystallised from acetone, it had m. p. 181·5—183° (Found: C*, 25·6; H*, 5·02; Cl†, 16·7; Pt†, 45·9%; *M*, ebullioscopic in 1·44% benzene solution, 837; in 2·72%, 859. $C_{18}H_{42}Cl_4P_2Pt_2$ requires C, 25·4; H, 5·0; Cl, 16·6; Pt, 45·9%; *M*, 853). It is readily soluble in cold benzene and chloroform, moderately soluble in cold acetone and alcohol, but insoluble in ligroin and dry ether. It is, however, soluble in wet ether. The same product is obtained when the above preparation is made from either the pure *cis*- or the pure *trans*-isomer.

Chlorination of cis-*Bis(tri-n-propylphosphine)dichloroplatinum* (I).—A carbon tetrachloride solution of chlorine (21·7 c.c.; 0·423 g. of Cl_2) was added to a benzene solution of (I) [90 c.c.; 3·5 g. of (I)] at 5—6°. The colourless solution became yellow, and on standing overnight fine yellow needles of *cis-bis-(tri-n-propylphosphine)tetrachloroplatinum* (IV) (1·74 g.) separated. It was recrystallised from alcohol rapidly (to minimise isomerisation); m. p. 123—127° (decomp.), resolidifying and remelting at 178—200° (Found: C‡, 32·8; H‡, 6·1%; *M*, ebullioscopic in 0·942% benzene solution, 555; in 1·66%, 578; in 0·89% acetone, 695; in 1·64%, 602. $C_{18}H_{42}Cl_4P_2Pt$ requires C, 32·9; H, 6·4%; *M*, 657·5). The benzene filtrate, after evaporation of the benzene at the pump, yielded a sticky residue from which 1·0 g. of the *trans*-isomer (V) was recovered by recrystallisation from acetone.

The above *cis*-platinic complex (IV) is most readily prepared by passing chlorine through the benzene solution of (I) with cooling, seeding the solution with (IV), immediately filtering off the crystalline precipitate, and recrystallising it from alcohol.

Chlorination of trans-*Bis(tri-n-propylphosphine)dichloroplatinum* (II).—When (II) (3 g.) was treated with chlorine (0·36 g.) as above, there was immediate deepening of colour and golden-yellow crystals separated. The mixture was evaporated under reduced pressure and the residue, recrystallised from acetone, yielded 2·28 g. of pure trans-*bis(tri-n-propylphosphine)tetrachloroplatinum*, m. p. 174—180° (decomp.) depending on the rate of heating (Found: C*, 32·9; C‡, 33·1; H*, 6·4; H‡, 6·15%; *M*, ebullioscopic in 1·08% benzene solution, 645; in 2·55%, 633; in 1·16% acetone 545; in 2·58%, 597. $C_{18}H_{42}Cl_4P_2Pt$ requires C, 32·9; H, 6·4%; *M*, 657·5). This compound is also most readily prepared by reaction of excess gaseous chlorine on a benzene solution of (II), followed immediately by evaporation under reduced pressure and treatment as above.

The solubilities of these two isomeric platinic complexes are as follows:

		Ether.	Alcohol.	Acetone.	Benzene.
cis	Cold	i	ss	vs	i
	Hot	i	vs	vs	vs
trans	Cold	i	ss	ss	vs
	Hot	i	ms	ms	vs

(i = insoluble, ss = slightly soluble, ms = moderately soluble, vs = very soluble.)

Chlorination of Dichlorobis(tri-n-propylphosphine)-μμ'-dichlorodiplatinum (III).—(III) (5 g.) in chloroform (100 c.c.) was chlorinated at 0° by slow addition of 30·4 c.c. of a carbon tetrachloride solution of chlorine (0·85 g. = 2 mols.) with shaking. The solution, from which some oil had separated, was kept for 5 minutes, and the chloroform then removed by distillation at 18 mm. pressure. The sticky orange residue was repeatedly extracted by long shaking with ether until the extract was colourless and a small quantity of sticky reddish-brown solid "A" remained. This extraction is slow and it is best if the ether is not quite anhydrous.

The ethereal solution was then evaporated to dryness at 15—20 mm. pressure, and the sticky yellow residue immediately extracted thrice with a little fresh dry ether to remove the very soluble part. A small residue of unoxidised (III) remained. The solution contained the main product, *diethyl ether–tri-n-propylphosphinetetrachloroplatinum*, $Et_2O,PPr^n_3,PtCl_4$, together with oily by-products, and the separation is rather difficult. Care must be taken not to decompose this etherate by excessive drying of ether

because the *hexachlorobis(tri-n-propylphosphine)-μμ'-dichlorodiplatinum* (VI) thus produced dissolves again only slowly in ether and will be removed mixed with unchanged (III).

The concentrated ethereal extract was evaporated to crystallisation at 15—20 mm. pressure. The yellow crystalline paste was pressed free from oily products on the filter and then washed with a very little ether. The solid etherate thus obtained was immediately dissolved in a little ether and caused to crystallise slowly by cautious addition of ligroin (b. p. 60—80°) until crystallisation just started. It was then set aside in an almost closed vessel so that slow evaporation of the ether caused large lemon-yellow crystals to develop during the course of about 6 hours. There was also a slight separation of gummy material, and this apparently coated some of the crystals with a very thin skin, thus preserving them from decomposition in air for some time (1—3 hours) after they had been removed from the solution. The crystals were therefore dried in air for 1½ hours and those which had not effloresced were analysed (Found: C‡, 26·2; H‡, 5·5; Pt‡, 34·3; loss on drying for 8 hours at 10^{-4} mm. Et_2O‡, 13·65. $C_{18}H_{42}OCl_4P_2Pt$ requires C, 27·3; H, 5·5; Pt, 34·2; Et_2O, 13·0%). On being heated, the compound reddens owing to loss of ether at 80—140°, and melts with decomposition at about 150°. It is very soluble in cold ether, acetone, hydroxylic organic solvents, and concentrated hydrochloric acid; it is less soluble in chloroform, slightly soluble in benzene, and insoluble in *cyclo*hexane and carbon tetrachloride. The hydrochloric acid solution deposits a yellow oil on dilution and this oil dissolves on further dilution. The dilute acid solution liberates iodine immediately on addition of potassium iodide.

The orange residue which remained after drying the etherate *in vacuo* as above was pure hexachlorobis(tri-n-propylphosphine)-μμ'-dichlorodiplatinum (VI), m. p. 150—151·5° (decomp.) (Found: C‡, 21·7; H‡, 4·4. $C_{18}H_{42}Cl_6P_2Pt_2$ requires C, 21·7; H, 4·2%). It is most easily obtained by dissolving the crude solid etherate, which has been freed from oil, in ether (0·5 g. in 3 c.c.), then reprecipitating it in the form of fine crystals by cautious addition of about an equal volume of ligroin. These crystals effloresce even during filtration and washing and lose all their ether on standing overnight over sulphuric acid in a vacuum desiccator to yield pure (VI). This substance is almost insoluble in all except oxygen-containing solvents. It dissolves in ethyl acetate, acetone, and alcohol, and slowly in ether to give yellow solutions, presumably containing complexes of a similar nature to the etherate. This was confirmed by taking the molecular weight of (VI) ebullioscopically in acetone. It was found to be approximately half the formula weight (Found: *M*, in 1·42% solution, 410; in 2·34%, 422. Calc. for ½($C_{18}H_{42}Cl_6P_2Pt_2$): *M*, 497].

The small quantity of sticky brown solid "A" (above) was extracted with chloroform to leave a residue of crude *tri-n-propylhydroxyphosphonium tetrachloro-μμ'-dichlorodiplatinite* $[PPr^n_3{\cdot}OH]^+_2[Pt_2Cl_6]^=$. This substance is very soluble in acetone, alcohol, and such solvents but insoluble in non-polar solvents. It was purified by solution in a minimum of methyl ethyl ketone, from which it could be caused to crystallise in fine reddish-brown needles by cautious addition of glacial acetic acid; yield 0·2 g. It had m. p. 150—159° (decomp.), and slowly became black in contact with ordinary air but was stable for about a month in dry air. It blackened during ½ hour at 80° *in vacuo* at 10^{-4} mm. pressure (Found: C†, 22·6; H†, 4·6; Cl†, 22·1, 22·2, 22·5; P†, 6·3; Pt†, 40·8, 40·7. $C_{18}H_{44}O_2Cl_4P_2Pt_2$ requires C, 22·6; H, 4·6; Cl, 22·2; P, 6·5; Pt, 40·8%).

It was further characterised by treatment of 0·166 g. in cold aqueous solution with tetrammino-platinous chloride, $Pt(NH_3)_4Cl_2.H_2O$, to form the chloride:

$$[PPr^n_3{\cdot}OH]_2Pt_2Cl_4 + 2Pt(NH_3)_4Cl_2 = 2PPr^n_3(OH)Cl + 2Pt(NH_3)_4PtCl_4\downarrow$$

This was too deliquescent to be isolated in so small a quantity as was obtained from the above reaction, but by addition of the theoretical quantity of hydrochloroplatinic acid, evaporation to dryness in a desiccator, and crystallisation of the residue from concentrated hydrochloric acid, the chloroplatinate was obtained in hydrated orange needles, m. p. 84—85° alone and mixed with an authentic specimen (see tri-n-propylphosphine hydroxy-salts, p. 2306). The green Magnus's salt obtained in the above reaction was identified by analysis (Found: N‡, 9·2. Calc. for $H_{12}N_4Cl_4Pt_2$: N, 9·3%).

Attempts to chlorinate (III) in benzene solution by using the theoretical quantity of chlorine in carbon tetrachloride solution were partly successful but an appreciable part of the chlorine was used in chlorinating the benzene because the chlorinated product is a very active catalyst for this chlorination. The use of an excess of chlorine gas causes rapid liberation of hydrogen chloride which destroys any (VI) produced, and solid products formed by chlorination of the benzene soon start to separate. This result is in marked contrast to the chlorination of simple tertiary phosphine and arsine derivatives which occurs cleanly in benzene solution.

Separation of the Simple Platinous and Platinic Chloride Complexes of Tri-n-propylphosphine, (I), (II), (IV), *and* (V).—In the following experiments it was necessary to separate mixtures of two or more of the above substances. This was easily accomplished by extraction with organic solvents according to the scheme below.

Solid mixture of (I), (II), (IV), *and* (V). Extract by shaking with cold benzene for one hour.

Residue. (IV) — *Filtrate contains* (I), (II), *and* (V). Evaporate to dryness at room temperature under reduced pressure, and extract the dry solids with as little cold MeOH as is judged necessary to dissolve (I) and (II).

Residue. (V) — *Filtrate contains* (I) *and* (II). Evaporate to dryness as above and extract with Et_2O.

Residue. (I) — *Filtrate contains* (II). Recover by evaporation.

If the original mixture of (I), (II), (IV), and (V) is sticky owing to the presence of other substances, the separation is not so clean as is indicated above. Interference occurs particularly at the extraction with methyl alcohol, which extracts some of (V) together with (I) and (II), so repeated extraction of later residues becomes necessary.

In the following experiments these compounds and the platinous bridged complex (III), whenever they were isolated, were identified by mixed m. p. with authentic specimens.

Isomerisation of cis-*Bis(tri-n-propylphosphine)tetrachloroplatinum* (IV).—(a) *In cold benzene.* The *cis*-platinic derivative (IV) (0·5 g.) was suspended in cold benzene (50 c.c.) and kept, with occasional shaking, for 5 days. The maximum room temperature was 17°. The unchanged *cis*-isomer (0·35 g.) was then filtered off, and the solution yielded 0·15 g. of crude *trans*-isomer. (b) *In boiling acetone.* The *cis*-platinic derivative (IV) (2·14 g.) in 50 c.c. of acetone was boiled for 55 minutes, then 25 c.c. were removed for analysis according to the above scheme. After a further 13 hours' boiling, the second 25 c.c. were also analysed. From the former, 0·86 g. of *cis*- and 0·21 g. of *trans*-isomer were recovered. In the second case no *cis*-isomer remained (cf. reduction by acetone).

Isomerisation of cis- *and* trans-*Bis(tri-n-propylphosphine)dichloroplatinum*, (I) *and* (II).—(a) *Isomerisation in a molten condition.* Samples of each platinous isomer were kept at about 160° and at 195° for 2½ hours. Isomerisation occurred as follows:

Temp.	Starting material.	Products, g. *cis*-.	Products, g. *trans*-.	Isomerisation, %.
160°	1·0 g., *cis*-	0·43	0·53	55
160	1·05 g., *trans*-	0·068	0·94	6·7
195	0·31 g., *cis*-	0·036	0·25	87
195	0·7 g., *trans*-	0·024	0·64	3·5

These approximate figures show that the equilibrium moves towards the side of *trans*-$(PPr_3)_2PtCl_2$ at higher temperatures, hence heat must be evolved in the change from *trans*- to *cis*-. It is intended to investigate this and similar equilibria further.

(b) *Attempted isomerisation in boiling acetone.* When 1 g. of the *cis*-platinous isomer in 15 c.c. of acetone was boiled for 15 hours, no isomerisation occurred and 0·95 g. of unchanged material was recovered.

Thermal Decomposition of the trans-*Platinic Complex* (V).—(V) (1 g.) was heated to 190° for 15 minutes. The temperature was then raised to 200° for 2 minutes to clarify the melt, and the product, a sticky brown oil, yielded a solid mixture of 0·12 g. of *trans*- and 0·08 g. of *cis*-$(PPr_3)_2PtCl_2$ on addition of a little alcohol and keeping overnight. In a repeat experiment the oil was first extracted with benzene but no residue of $[PPr_3Cl]_2PtCl_4$ remained (cf. next experiment).

Thermal Decomposition of the cis-*Platinic Complex* (IV).—(IV) (1·54 g.) was kept at 135—140° for 10 minutes, then cooled, and the product extracted with benzene. A residue of buff-coloured solid " B " remained. Analysis of the benzene solution according to the scheme on p. 2307 yielded the *trans*-platinic complex (V) (0·67 g.), the *cis*-platinous complex (I) (0·13 g.), and the *trans*-platinous complex (II) (0·23 g.). The substance " B " is a salt, very soluble in water and alcohol. It was recrystallised thrice from very little concentrated hydrochloric acid with final cooling in ice-water. The solubility of the salt increases so rapidly in the range 0—20° that it is essential to keep the solution cold and filter it through a well-cooled funnel. In this way pure tri-*n*-propylhydroxyphosphine chloroplatinate $[PPr_3OH]_2[PtCl_4].2H_2O$ was obtained in well-formed efflorescent orange needles. It had m. p. 84—85° alone and mixed with the synthetic specimen (see below). This material was also converted into the platinite, m. p. 100—102° (decomp.) alone and mixed with a synthetic specimen (see below).

Tri-n-propylhydroxyphosphonium Salts.—Direct synthesis. Chlorine (1·13 g.) in glacial acetic acid (43·7 c.c.) was run into a solution of tri-*n*-propylphosphine (2·5 g.) in glacial acetic acid (15 c.c.) with ice-cooling. To this solution was immediately added $H_2PtCl_6.4{\cdot}05H_2O$ (3·77 g.) in the acid (10 c.c.). A red oil separated and was caused to crystallise by seeding with the chloroplatinate " B " from the above preparation. It was twice recrystallised as above from concentrated hydrochloric acid, and the crystals were air-dried for 4½ hours. Crystals which had not effloresced were analysed. *Tri-n-propylhydroxyphosphonium chloroplatinate* thus obtained had m. p. 84—85° (Found: C, 27·1; H, 6·05. $C_{18}H_{44}O_2Cl_6P_2Pt$ requires C, 27·1; H, 6·06%).

The chloroplatinite was prepared as follows. Potassium chloroplatinite (0·39 g.) in water (2 c.c.) was mixed with a cold solution of the hydroxy-chloroplatinate (0·75 g., 1 mol.) in water (8 c.c.) and the precipitated potassium chloroplatinate removed. The aqueous filtrate was evaporated to dryness in a vacuum desiccator over sulphuric acid, and the residue extracted with alcohol, leaving a small residue of potassium chloroplatinate. The alcoholic extract was evaporated to dryness at 15 mm. pressure, and the residue, thrice recrystallised from acetone, yielded pure *tri-n-propylhydroxyphosphonium chloroplatinite*, m. p. 101—102° (decomp.) dependent on the rate of heating (Found: Cl, 31·1; H, 6·35; O, 5·03. $C_{18}H_{44}O_2Cl_4P_2Pt$ requires C, 31·3; H, 6·4; O, 4·6%).

Reduction of the Platinic Complexes (IV, V, VI).—(a) *With potassium iodide.* 5—10 Mg. of each solid were ground with 2—3 c.c. of potassium iodide solution containing starch. A faint violet colour developed with the *cis*-isomer (IV) after 5—10 minutes. No change at all occurred with the *trans*-isomer. A violet colour developed immediately with the bridged complex (VI), becoming almost black after 10 minutes. A drop of thiosulphate solution decolourised the solution from both (IV) and (VI).

(b) *With boiling acetone.* The *cis*-platinic complex (IV) (1·07 g.) in 25 c.c. of acetone was boiled under reflux for 14 hours, then concentrated to about 5 c.c.; 0·41 g. of *trans*-$(PPr_3)_2PtCl_4$ crystallised out and

was removed. The filtrate was evaporated to dryness, and the sticky residue analysed according to the scheme on p. 2307. No *cis*-platinic (IV) or *cis*-platinous (I) complexes could be detected, but 0·05 g. of *trans*-platinous complex (II) was isolated. A sticky residue remained. Because the *cis*-complexes are most easily isolated and purified, we can be certain that the quantity here, if any, is negligible, but the residue undoubtedly contained more of both the *trans*-complexes. It seems probable that, by-products being ignored, 90% isomerisation and 10% reduction to the *trans*-platinous complex represents the course of this reaction.

The *trans*-platinic complex (V) (2·5 g.) was similarly treated; 2·32 g. of unchanged material was recovered and no other platinous or platinic complexes were detected in the small sticky residue.

The bridged platinic complex (VI) (0·3 g.), similarly treated in 10 c.c. of acetone, blackened rather rapidly, so after 4 hours it was evaporated to yield a black pasty oil from which 0·06 g. of pure bridged platinous complex (III) was obtained by washing away the oil with a very little acetone.

(c) *With sulphur dioxide in aqueous acetone.* The *cis*-platinic complex (IV) (0·9 g.) in 110 c.c. of acetone and 30 c.c. of water was treated with 0·105 g. of sulphur dioxide (20% excess) in 10 c.c. of acetone and kept for 4½ days. The acetone and excess of sulphur dioxide were removed at 15 mm. pressure, and the solid (0·61 g.) which separated from the aqueous solution was filtered off. The pale yellow aqueous solution gave a slight test for sulphate and contained acid sulphito-platinum complexes which were not investigated. The water-insoluble solid was analysed according to the above scheme and contained 0·08 g. of unchanged *cis*-platinic complex, 0·32 g. of *trans*-platinic complex, 0·13 g. of *cis*-platinous complex, and 0·03 g. of *trans*-platinous complex.

The *trans*-platinic complex (0·73 g.) in 60 c.c. of acetone and 4 c.c. of water was similarly treated with 0·085 g. of sulphur dioxide in 15 c.c. of acetone. 0·63 G. of water-insoluble material, from which were obtained 0·55 g. of pure unchanged *trans*-platinic complex and 0·02 g. of *trans*-platinous complex, but no *cis*-isomers, was recovered. The aqueous solution from this experiment was not coloured and gave only the faintest test for sulphate.

The bridged platinic complex (VI) (0·3 g.) in 25 c.c. each of acetone and water was treated with 0·075 g. of sulphur dioxide in 10 c.c. of acetone and kept for 5 days. Evaporation of the solution as above yielded 0·31 g. of water-insoluble material. The aqueous solution gave a good test for sulphate. The 0·31 g. of solid yielded a residue of 0·13 g. of the platinous bridged complex (III) by extraction with a little acetone, and the acetone extract was taken to dryness. The residue from the extract was dissolved in ether and 0·02 g. of *p*-toluidine added. This caused *p*-toluidine–tri-*n*-propylphosphinetetrachloroplatinum to separate, m. p. 144—145° (decomp.), indicating that the acetone-soluble part of the 0·31 g. of solid was largely unreduced starting material.

(d) *With stannous chloride.* Hydrated stannous chloride (0·53 g.) in water and acetone (5 c.c. each) containing one drop of concentrated hydrochloric acid was gradually added at room temperature to a solution of 1·5 g. of *cis*-platinic complex (IV) in 20 c.c. of acetone and 3 c.c. of water. The solution became paler, with a transient orange coloration, as each addition was made. The solution was now warmed to 40—50° for 10 minutes and then kept at room temperature for ½ hour. The acetone was removed at 15 mm. pressure, and the remaining aqueous suspension filtered. The solid (1·11 g.) thus obtained yielded 0·72 g. of *cis*- and 0·39 g. of *trans*-platinous isomers (I and II).

When the *trans*-platinic complex (V) (1·5 g.) in 115 c.c. of acetone (it is less soluble than the *cis*-isomer) was similarly treated with an identical solution of stannous chloride, the solution became paler and after addition of a little water it was worked up as above. 1·32 G. of solid were recovered which, by analysis as above, contained 0·32 g. of unchanged *trans*-platinic complex, 0·13 g. of *cis*-, and 0·74 g. of *trans*-platinous complexes (I and II).

The platinic bridged complex (VI) (0·3 g.) in 4 c.c. of acetone and 0·6 c.c. of water, similarly treated, reddened at once when the addition of stannous chloride was made. The colour faded slowly at room temperature but rapidly and completely on warming. Worked up as above, 0·26 g. of water-insoluble solid was recovered. This was separated by recrystallisation from ethyl acetate into 0·13 g. of pure bridged platinous complex (III) and a sticky intractable residue.

Reaction of p-*Toluidine with the Platinous Bridged Complex* (III).—*p*-Toluidine (0·27 g., 1·05 mols.) in benzene (3 c.c.) was added to a solution of (III) (1 g.) in benzene (30 c.c.). The colour changed immediately from orange to yellow. The solution was evaporated to dryness at 15 mm. pressure, and the residual yellow oil (0·2 g.) crystallised at once on addition of ether. Careful fractionation of the product from methyl alcohol showed that only one geometric isomer was present, presumably of *trans*-configuration [compare the reaction of PPr_3 with (III), p. 2306]. trans-p-*Toluidine–tri-n-propylphosphinedichloroplatinum* (X) is thus obtained in lemon-yellow prisms, m. p. 110·5—111·5° (Found: C, 36·1; H, 5·7%; *M*, ebullioscopic in benzene, in 1·36% solution 470; in 2·16%, 485. $C_{15}H_{35}NCl_4PPt$ requires C, 36·0; H, 5·7%; *M*, 533).

Reaction of p-*Toluidine with the Etherate from the Platinic Bridged Complex* (VI).—Diethyl ether–tri-*n*-propylphosphinetetrachloroplatinum (0·9 g.) in ether (9 c.c.) was treated with *p*-toluidine (0·16 g.) in ether (4 c.c.). Golden-yellow crystals started to separate at once, and after 24 hours were filtered off. One recrystallisation from alcohol gave 0·51 g. of pure p-*toluidine–tri-n-propylphosphinetetrachloroplatinum* (XI), m. p. 147—151° (decomp.) (Found: C†, 31·5; H†, 5·1. N†, 2·4; Cl†, 23·4; Pt†, 32·2%; *M*, ebullioscopic in benzene, in 1·48% solution, 560; in 1·96% solution, 540; in 1·23%, 550; in 2·00%, 573. $C_{19}H_{36}NCl_4PPt$ requires C, 31·9; H, 5·0; N, 2·3; Cl, 23·4; Pt, 32·2%; *M*, 604). Because of the lability of platinic complexes this substance must have a *trans*-configuration.

Chlorination of p-*Toluidino–tri-n-propylphosphinedichloroplatinum* (X).—(X) (1·42 g.) in benzene (15 c.c.) was treated with chlorine (0·189 g.) in carbon tetrachloride solution (3·29 c.c.) with ice-cooling, and kept for 40 minutes. The solution was now evaporated to dryness under 15 mm. pressure, leaving

a residue of 1·64 g. of sticky crystalline solid. Twice recrystallised from ethyl alcohol, it yielded pure *p*-toluidine-tri-*n*-propylphosphinetetrachloroplatinum (0·76 g.), m. p. 147—151° (decomp.) alone and mixed with an authentic specimen.

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472. *A Study of Diazo-compounds by Use of Nitrogen Isotopes. Part I. The Structure of the Diazonium Ion.*

By P. F. HOLT and (MISS) B. I. BULLOCK.

The non-equivalence of and absence of interchange between the nitrogen atoms of a diazonium ion has been demonstrated by diazotising isotopically labelled aniline, coupling the diazonium salt, and regenerating the aniline by reduction of the azo-compound.

THE diazonium ion is considered to have a structure similar to that of the ammonium ion but with an atom of nitrogen replacing three hydrogen atoms, a structure requiring the non-equivalence of the two nitrogen atoms. This non-equivalence has been demonstrated experimentally as a preliminary stage in the study of diazo-compounds in which one nitrogen atom is isotopically labelled.

A diazonium salt prepared from ^{15}N-labelled aniline and unlabelled sodium nitrite, was coupled with 2-naphthol. The amine hydrochlorides formed when the resulting azo-compound was reduced were separated, and a sample of nitrogen from each was prepared and analysed in the mass spectrograph. The complete synthesis was thrice repeated. In two of these later

Expt.	1 (preliminary run).	2.	3.	4.
Time between diazotisation and coupling (hrs.)	0	0	8	24
Aniline hydrochloride: ^{15}N atom-% excess	31·33	32·47	32·43	32·74
1-Amino-2-naphthol hydrochloride: ^{15}N atom-% excess ...	1·628	3·987	2·072	1·777

Atom-% ^{15}N in phthalimide: Found, 32·36.

experiments the diazonium salt was stored for several hours at 0° before coupling so that any slow interchange between the nitrogen atoms might become apparent. The analyses (see Table) suggest that the reactions proceed according to the scheme shown and that interchange is absent or immeasurable.

$$Ph\cdot{}^{15}NH_2 \xrightarrow{NaNO_2\text{-}HCl} [Ph\cdot{}^{15}N{:}N]^+ \xrightarrow{2\text{-Naphthol}} Ph\cdot{}^{15}N{:}N\cdot C_{10}H_{10}\cdot OH \xrightarrow[HCl]{SnCl_2}$$

$$Ph\cdot{}^{15}NH_2 + NH_2\cdot C_{10}H_6\cdot OH(2:1)$$

Labelled aniline has been previously synthesised by Allen and Wilson (*J. Amer. Chem. Soc.*, **1943**, **65**, 611) and by Fones and White (*Arch. Biochem.*, **1949**, **20**, 118) from ammonia. The yield from phthalimide (92%) is similar to that obtained by Fones and White from ammonia, and the route described may be preferable because of its simplicity.

EXPERIMENTAL.

Labelled Anthranilic Acid.—Potassium phthalimide (1·00 g.; ^{15}N atom-% excess nominally **33**), followed immediately by sodium hydroxide (1·07 g. in 3·3 ml. of water), was added to cold hypobromite solution (0·4 ml. of bromine added to 1·2 g. of sodium hydroxide in 5 ml. of water at 0°). The solution was heated for 2 minutes at 80°, cooled in ice, and neutralised by dropwise addition of hydrochloric acid (approx. 2·5 ml.). The anthranilic acid was precipitated by 1 ml. of glacial acetic acid, filtered off (filter-stick), washed with water, and vacuum-dried. It was not purified.

Labelled Aniline.—The anthranilic acid was transferred to a bulb-to-bulb distillation unit and kept at 210° in an electrically heated block. Aniline distilled into the cool bulb (yield, 0·46 g.).

Labelled 1-Benzeneazo-2-naphthol.—The aniline was dissolved in 2 ml. of diluted hydrochloric acid (1 : 1) and 40% sodium nitrite solution was added dropwise until free nitrous acid was detected. The solution was added to 0·6 g. of 2-naphthol in 3 ml. of 10% sodium hydroxide, and the precipitated azo-compound was filtered off, washed with water, and vacuum-dried (0·83 g., crude).

Reduction.—The 1-benzeneazo-2-naphthol, in alcohol (10 ml.), was boiled under reflux for 30 minutes with stannous chloride (2 g.) in concentrated hydrochloric acid (6 ml.) and the solution was decanted. On cooling, 1-amino-2-naphthol hydrochloride crystallised and was separated by aid of a filter-stick (0·45 g.). The filtrate was made alkaline and steam-distilled. From the acidified and concentrated distillate aniline hydrochloride crystallised (0·106 g.), m. p. 196—198°. Nitrogen samples for mass-spectrographic analysis were prepared from the amines (Rittenberg, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Michigan, 1948, p. 31).

Discussion.

The synthesis of labelled compounds must necessarily be carried out on small quantities, and the final yields in the present series were small. From the reduction mixture of amines, separation of pure aniline is readily accomplished by steam-distillation, but complete purification of the amino-naphthol is impracticable on the small quantities involved. The values for the isotope ratios in the regenerated aniline were consistent; those for the aminonaphthol were less so, owing, presumably, to contamination of the aminonaphthol with aniline. The results in the table show that the nitrogen in the regenerated aniline had a similar isotope ratio to that of the starting material. This confirms the non-equivalence of the nitrogen atoms in the diazonium group, demonstrates the absence of interchange between them, and proves that the diazonium group is attached to the phenyl group throughout the synthesis.

We are indebted to the Mass Spectrometer Group, Atomic Energy Research Establishment, Harwell, who assayed our nitrogen samples, and to the Department of Scientific and Industrial Research for a grant to one of us (B. I. B.).

The University, Reading. [*Received, June 2nd,* 1950.]

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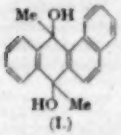
473. *Substituted Anthracene Derivatives. Part II. An Example of* 1 : 5-*Anionotropic Rearrangement.*

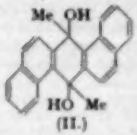
By G. M. Badger and R. S. Pearce.

The acid-catalysed dehydration of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (I), in the presence of an alcohol, has been shown to give 9-methyl-10-alkoxy-methyl-1 : 2-benzanthracene (VI). The formation of this substance involves a 1 : 5-anionotropic rearrangement of the initial product of dehydration (V), and alkylation with the alcohol used as solvent.

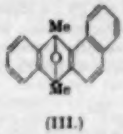
When a solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (I) in warm methanol was treated with a little sulphuric acid, a mixture of the expected methyl ether and a dehydration product was obtained (Badger, Goulden, and Warren, *J.*, 1941, 18). A similar product of dehydration was obtained by treatment of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene (II) with boiling alcoholic picric acid. The dehydration products were tentatively assigned the structures of endocyclic monoxides (III and IV), by analogy with that proposed by Enderlin (*Compt. rend.*, 1936, **202**, 669, 1188) for the product of thermal dehydration of 6 : 12-dihydroxy-6 : 12-diphenyl-5 : 11-di-*p*-bromo-



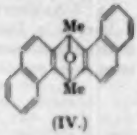
(I.)



(II.)



(III.)



(IV.)

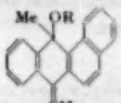
phenyl-6 : 12-dihydronaphthacene. Structures involving transannular monoxide bridges have also been proposed for the compound obtained by reduction of rubrene photo-oxide with zinc and acetic acid, for the isomerisation product of the same photo-oxide (Bergmann and McLean, *Chemical Reviews*, 1941, **28**, 367), and for the dehydration product of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene (Guyot and Staehling, *Bull. Soc. chim.*, 1905, **33**, 1144). None of these structures is at all probable for these compounds. Although models of transannular *per*-oxides can be constructed without strain (Dufraisse, *Bull. Soc. chim.*, 1939, **6**, 422), dihydro-aromatic structures having a *mono*-oxide bridge involve very considerable distortion of the normal valency angles for both oxygen and carbon.

The study of the structures of these supposed *endo*monoxides has now been undertaken, and the present paper records the results of an investigation into the nature of the product obtained from the diol (I) by warm methanol and sulphuric acid. Satisfactory conditions for the preparation of this product in good yield by the addition of a little concentrated hydrochloric acid to a boiling methanolic solution of the diol have been devised.

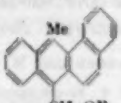
It soon became evident that this product cannot have the *endo*monoxide structure (III) as its properties are not consistent with its being a dihydrobenzanthracene derivative. Even when highly purified it is faintly yellow, and its solutions show a strong blue fluorescence. Moreover, it forms a dark red picrate. When tested for carcinogenic activity (under the name "9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene 9 : 10-oxide") it was found to be moderately active, although the corresponding *endo*peroxide (photo-oxide) is inactive, as expected (Badger *et al.*, *Proc. Roy. Soc.*, 1940, *B*, **129**, 445). These properties are those expected of a fully aromatic *meso*-substituted benzanthracene derivative; this structure was also indicated by the rate of addition of osmium tetroxide, which was intermediate between those for 1 : 2-benzanthracene and 9 : 10-dimethyl-1 : 2-benzanthracene (cf. Badger, *J.*, 1949, 456).

The endocyclic monoxide structure (III) was finally rejected when it was found that the product obtained by dehydration of the diol (I) in ethanol is similar to, but not identical with, that obtained in methanol. It has now been established that dehydration of the diol (I) in methanol gives 9-methyl-10-methoxymethyl-1 : 2-benzanthracene (VI; R = Me), and that dehydration in ethanol gives the 10-ethoxymethyl analogue (VI; R = Et). These products can only be formed if the initial dehydration product (V; R = H) or its alkyl ether (V; R = Me or Et) suffers 1 : 5-anionotropic rearrangement.

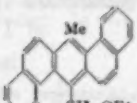
The structure of the product (VI; R = Me) has been confirmed by direct comparison with a specimen obtained by iodomethylation of 9-methyl-1 : 2-benzanthracene, followed by treatment with sodium methoxide (Sandin and Fieser, *J. Amer. Chem. Soc.* 1940, **62**, 3098). Similarly,



(V.)



(VI.)

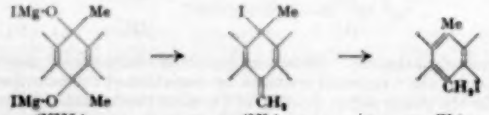


(VII.)

dehydration of the diol (I) with boiling ethanolic picric acid gave 9-methyl-10-ethoxymethyl-1 : 2-benzanthracene (as the picrate) identical with a specimen prepared as above but with sodium ethoxide. The ultra-violet absorption spectrum of this compound resembled that of 9 : 10-dimethyl-1 : 2-benzanthracene (Fig. 1).

There can be no doubt that 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene (II) also suffers dehydration and rearrangement with alkylation when heated with alcoholic picric acid (Badger, Goulden, and Warren, *loc. cit.*). The compound previously regarded as 9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene 9 : 10-oxide (IV) must therefore be 9-methyl-10-ethoxymethyl-1 : 2 : 5 : 6-dibenzanthracene (VII), and the ultra-violet absorption spectrum is consistent with this conclusion (Fig. 2).

1 : 5-Anionotropic shifts are by no means unknown in the anthracene series. For example, Julian, Cole, Diemer, and Schafer (*ibid.*, 1949, **71**, 2058) found that 9-hydroxy-10-benzylidene-9 : 10-dihydroanthracene is readily rearranged to 9-α-hydroxybenzylanthracene by brief boiling in acetone solution with a little sulphuric acid. Similarly, 9-hydroxy-9-phenyl-10-benzylidene-

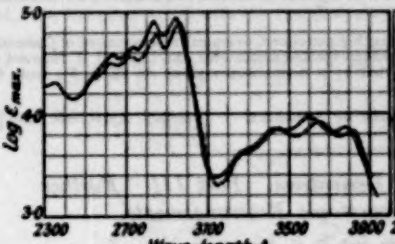


9 : 10-dihydroanthracene is isomerised to 9-phenyl-10-α-hydroxybenzylanthracene (Julian and Cole, *ibid.*, 1935, **57**, 1609, who give references to earlier work by Barnett and Cook). It is also noteworthy that Sandin and Fieser (*loc. cit.*) have prepared 9-methyl-10-iodomethyl-1 : 2-benzanthracene (X) by addition of hydrogen iodide to the magnesium complex (VIII) from

1 : 2-benzanthraquinone and methylmagnesium iodide. The intermediate (IX) evidently undergoes anionotropic rearrangement to give the iodomethyl compound (X).

Absorption spectra.

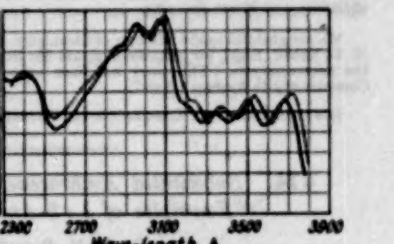
FIG. 1.



——— 9-*Methyl*-10-*ethoxymethyl*-1 : 2-*benzanthracene* (*in alcohol*) : *Maxima at* 2650 (4·59); 2745 (4·66); 2835 (4·91); 2945 (4·97); (3280, 3·83); 3440 (3·87); 3600 (3·98) 3765 A. (3·88) (*log ε in parentheses*).

– – – – 9 : 10-*Dimethyl*-1 : 2-*benzanthracene* (*after Jones*, J. Amer. Chem. Soc., 1945, **67**, 2127).

FIG. 2.



——— 9-*Methyl*-10-*ethoxymethyl*-1 : 2 : 5 : 6-*dibenzanthracene* (*in alcohol*) : *Maxima at* 2420 (4·36); (2800, 4·64); 2955 (4·87); 3070 (4·93); (3200, 4·08); 3350 (4·0); 3500 (4·11); 3680 A. (4·11) (*log ε in parentheses*).

– – – – 9 : 10-*Dimethyl*-1 : 2 : 5 : 6-*dibenzanthracene* (*after Maynecord and Roe*, Proc. Roy. Soc., 1935, *A*, **152**, 299).

EXPERIMENTAL.

9 : 10-*Dihydroxy*-9 : 10-*dimethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*.—The following modified method (cf. Davies and Kipping, *J.*, 1911, 296) was more satisfactory than the published procedure (Bachmann and Chemerda, *J. Amer. Chem. Soc.*, 1938, **60**, 1023). A mixture of benzanthraquinone (5 g.), magnesium (2·5 g.), methyl iodide (6 c.c.), dry benzene (30 c.c.), and dry ether (30 c.c.) was allowed to react. After 40 minutes, the reflux was maintained for a further hour by gentle heating. After cooling, the complex was poured into an ice-cold saturated solution of ammonium chloride. The ether–benzene layer deposited the diol (3·0 g.) when kept in the refrigerator overnight, and a further quantity (1·0 g.) was obtained by evaporation.

9-*Methyl*-10-*methoxymethyl*-1 : 2-*benzanthracene*.—(i) The formation of this compound, as a by-product in the preparation of 9 : 10-dimethoxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene, was first described (under the name " 9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene 9 : 10-oxide ") by Badger, Goulden, and Warren (*loc. cit.*). The published analytical figures are in good agreement with the structure now established (Found : C, 88·2; H, 6·3. Calc. for $C_{21}H_{18}O$: C, 88·1; H, 6·3%).

(ii) A solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (2 g.) in boiling methanol (40 c.c.) was treated with concentrated hydrochloric acid (8 c.c.). After 3 minutes, the solution was poured into water, and the product collected. 9-Methyl-10-methoxymethyl-1 : 2-benzanthracene crystallised from alcohol in pale yellow blades, m. p. 120—121°, alone or mixed with a specimen prepared by the first method.

(iii) The *picrate* of 9-methyl-10-methoxymethyl-1 : 2-benzanthracene was prepared from the diol by 2 hours' boiling with methanol and excess of picric acid. It formed small red needles, m. p. 108—109°, after recrystallisation from benzene (Found : C, 63·2; H, 3·9. $C_{21}H_{18}O,C_6H_3O_7N_3$ requires C, 62·9; H, 4·1%). Decomposition of the picrate in the usual way gave methylmethoxymethylbenzanthracene, m. p. 120—121°, alone or mixed with a specimen prepared by method (i).

(iv) 9-Methyl-10-methoxymethyl-1 : 2-benzanthracene was also prepared from 9-methyl-1 : 2-benzanthracene by iodomethylation to 9-methyl-10-iodomethyl-1 : 2-benzanthracene, followed by treatment with sodium methoxide (Sandin and Fieser, *loc. cit.*). A specimen, m. p. 120—121°, thus prepared showed no depression of the m. p. when mixed with specimens prepared by methods (i) and (ii). The same product was also obtained by treatment of the Grignard complex between 1 : 2-benzanthraquinone and methylmagnesium iodide with hydriodic acid, followed by treatment of the resulting iodomethyl compound with sodium methoxide (Sandin and Fieser, *loc. cit.*).

9-*Methyl*-10-*methoxymethyl*-1 : 2-*benzanthracene Photo-oxide*.—A solution of the above methylmethoxymethylbenzanthracene in benzene was set aside in diffuse sunlight in an open beaker for 3 days. Purification of the resulting dark brown sticky solid by recrystallisation from alcohol (charcoal) gave the *photo-oxide* as small colourless plates, m. p. 147—149° (Found : C, 79·0; H, 5·95. $C_{21}H_{18}O_2$ requires C, 79·2; H, 5·7%).

9-*Methyl*-10-*ethoxymethyl*-1 : 2-*benzanthracene*.—A solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (5 g.) and picric acid (10 g.) in absolute alcohol (1 l.) was boiled under reflux for 2 hours. After concentration and cooling, the picrate separated. This dissociated to some

extent on recrystallisation from alcohol and a pure specimen could not be obtained for analysis. The crude material had m. p. 83°. The picrate, in benzene, was decomposed by shaking it with aqueous sodium carbonate solution. 9-Methyl-10-ethoxymethyl-1 : 2-benzanthracene formed pale yellow blades, m. p. 126—127°, after recrystallisation from benzene (Found: C, 88·35; H, 6·7. Calc. for $C_{22}H_{20}O$: C, 88·0; H, 6·7%). The m. p. was not depressed by admixture with a specimen prepared by refluxing 9-methyl-10-iodomethyl-1 : 2-benzanthracene with sodium ethoxide in ethanol, according to the method of Sandin and Fieser (*loc. cit.*).

We are grateful to the Director of Chemistry, South Australian Government Department of Chemistry (S. D. Shield, Esq.), for permission to use the Beckman spectrophotometer, and to Mr. R. T. Howard for the microanalyses. This work has been supported by a maintenance grant (to R. S. P.) from the Commonwealth Research Fund.

JOHNSON CHEMICAL LABORATORIES, UNIVERSITY OF ADELAIDE. [*Received, April 19th*, 1950.]

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474. *Substituted Anthracene Derivatives. Part III. Further Examples of* 1 : 5-*Anionotropic Rearrangements.*

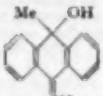
By G. M. BADGER and R. S. PEARCE.

When treated with acids in the presence of an alcohol as solvent, 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene (Ia) is converted into 9-methyl-10-alkoxymethylanthracene (IV) by 1 : 5-anionotropic rearrangement of the initial product of dehydration, and alkylation with the alcohol. The structure of the product (IV; R = Me) has been confirmed by comparison with a specimen prepared by another method.

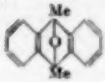
Similar treatment of 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (XIV) gave 9-benzyl-10-α-ethoxybenzylanthracene (XV), which has also been prepared from 9-formyl-10-benzylanthracene (XVII).

It has long been known that 9 : 10-dihydroxy-9 : 10-dialkylanthracenes (I) are particularly susceptible to dehydration, for by-products formed in this way have often been encountered after reaction of alkylmagnesium halides with anthraquinone. According to Guyot and Staehling (*Bull. Soc. chim.*, 1905, **33**, 1144) dehydration takes place in the presence of excess of the Grignard reagent, but this result was not, apparently, observed by Bachmann and Chemerda (*J. Org. Chem.*, 1939, **4**, 585), and it has not been confirmed in the present work. Dehydration is most easily effected by acids; to avoid it, the Grignard complexes must be decomposed with ammonium chloride. The structures of the dehydration products have never been established. Guyot and Staehling (*loc. cit.*) found that, when 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene (Ia) is boiled with acetic acid, a bright yellow, sparingly soluble substance corresponding to a mono-dehydration product is formed. The structures (II) and (III) were suggested, but neither is in accord with the properties of this compound.

(Ia, R = H; Ib, R = Me.)



(II.)

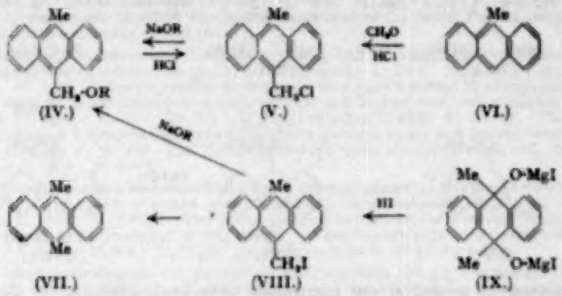


(III.)

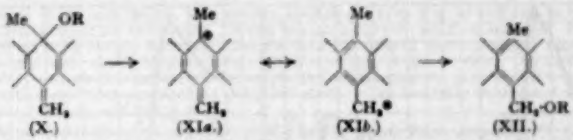
Guyot and Staehling also isolated a product, $C_{30}H_{24}O$, after treatment of the diol (Ia) with acetic acid containing mineral acid. Clarke and Carleton (*J. Amer. Chem. Soc.*, 1911, **33**, 1966) obtained two supposedly bimolecular compounds by dehydration of the diol (Ib). Little systematic work has been published on the dehydration of diols of type (I). As a preliminary step, we therefore examined the nature of the products obtained by acid-catalysed dehydration in an alcohol as solvent, concurrently with the study (preceding paper) of the structure of the product obtained by similar treatment of dimethylbenzanthraquinol.

It has now been established that when a boiling alcoholic solution of the diol (Ia) is treated with acid, the dehydration is accompanied by 1 : 5-anionotropic rearrangement and alkylation with the alcohol used as solvent. With a little hydrochloric acid in boiling methanol the diol (Ia) gave 9-methyl-10-methoxymethylanthracene (IV; R = Me) in good yield. In ethanol 9-methyl-10-ethoxymethylanthracene (IV; R = Et) was obtained, and in *n*-propanol 9-methyl-10-*n*-propoxymethylanthracene (IV; R = Pr^n). Mineral acid is not essential for this conversion, as picric acid is effective, giving rise to the corresponding picrates.

The mechanism of these rearrangements is of interest. It is possible that the initial step is one of alkylation by the alcohol used as solvent, and that the subsequent steps involve elimination of alcohol rather than dehydration. This seems to be indicated by the observation that 9 : 10-dimethoxy-9 : 10-dimethyl-9 : 10-dihydroanthracene, as well as the free diol, is converted into 9-methyl-10-methoxymethylanthracene when boiled with methanol and picric acid. On the other hand, with the free diol, alkylation may take place at a later stage in the



rearrangement. In any case, elimination of water or alcohol would be expected to give the intermediate compound (X; R = H or alkyl). Further elimination of an hydroxyl or alkoxyl radical, under the influence of the acid, would give rise to the mesomeric ion (XI). As pointed



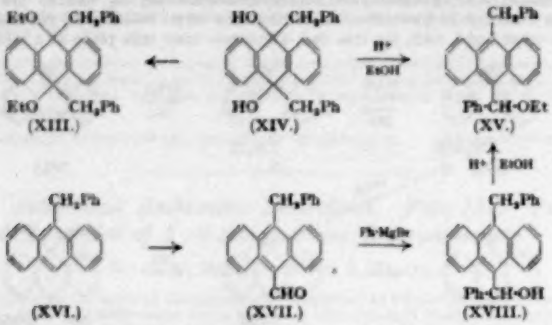
out by Dewar ("The Electronic Theory of Organic Chemistry," 1949, p. 88) when discussing a similar rearrangement in the polyene series, the alkoxyl radical would tend to recombine with the terminal carbon atom of the mesomeric ion, so that the fully aromatic structure (XII) is formed.

It was pointed out by Badger and Pearce (*loc. cit.*) that the preparation of 9-methyl-10-iodomethyl-1 : 2-benzanthracene by the action of hydrogen iodide on the magnesium complex from 1 : 2-benzanthraquinone and methylmagnesium iodide (Sandin and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 3098) also provides an example of a similar rearrangement under the influence of an acid. The corresponding rearrangement has now been carried out in the anthracene series. Addition of hydrogen iodide to the complex from anthraquinone and methylmagnesium iodide gave 9-methyl-10-iodomethylanthracene (VIII), which was, however, too unstable to permit purification. The structure of (VIII) was established by its reduction to 9 : 10-dimethylanthracene, and as treatment with sodium methoxide gave the substance (IV; R = Me) the structure of this too is established.

To confirm its structure (IV; R = Me) was also prepared from 9-methylanthracene (VI) by conversion with paraformaldehyde and hydrogen chloride in glacial acetic acid (cf. Badger and Cook, *J.*, 1939, 802) into 9-methyl-10-chloromethylanthracene (V), which was then treated with sodium methoxide. 9-Methyl-10-chloromethylanthracene was also obtained from (IV; R = Me) by dry hydrogen chloride in benzene.

The readiness with which diols of type (I) undergo the dehydration and rearrangement evidently depends on the nature of the alkyl or aralkyl group. With boiling alcoholic picric acid 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (XIV) gave only 9 : 10-diethoxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (XIII), but prolonged boiling with ethanol and mineral acid gave the expected dehydration product, 9-benzyl-10-α-ethoxybenzylanthracene (XV). In order to establish the structure of this transformation product, a series of reactions analogous to those used by Julian, Cole, Diemer, and Schafer (*J. Amer. Chem. Soc.*, 1949, **71**, 2058) was carried out. 9-Benzylanthracene was converted by Fieser's formanilide method (*Org. Synth.*,

1940, **20**, 11) into 9-formyl-10-benzylanthracene (XVII) and thence by phenylmagnesium bromide into 9-benzyl-10-α-hydroxybenzylanthracene (XVIII). With ethanol and a trace of sulphuric acid, this gave 9-benzyl-10-α-ethoxybenzylanthracene (XV).



The structures of several of our compounds have been confirmed by their ultra-violet absorption spectra (Figs. 1 and 2). 9-Methyl-10-ethoxymethyl- and 9-benzyl-10-α-ethoxy-

Fig. 1. Fig. 2.

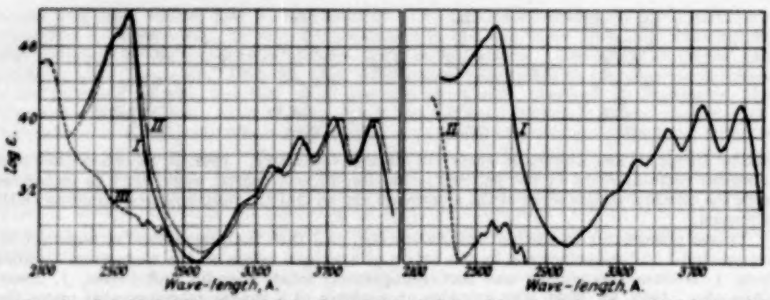


Fig. 1.—*I*, 9-*Methyl*-10-*ethoxymethylanthracene* (*in alcohol*). *Max.* (*and log ε*) *at* 2520 (4·93), 2590 (5·24), (3100, 2·69), (3250, 3·08), 3390 (3·48), 3550 (3·80), 3740 (4·01), (3870, 3·71), and 3950 (3·98). *II*, 9 : 10-*Dimethylanthracene* (*after Jones*, J. Amer. Chem. Soc., 1945, **67**, 2127). *III*, 9-*Methyl*-10-*ethoxymethylanthracene photo-oxide* (*in alcohol*).

Fig. 2.—*I*, 9-*Benzyl*-10-α-*ethoxybenzylanthracene* (*in alcohol*). *Max. and log ε at* (2550, 4·90), 2610 (5·20), (3110, 2·74), (3250, 3·18), 3400 (3·56), 3570 (3·90), 3760 (4·16), and 3980 (4·16). *II*, 9 : 10-*Diethoxy*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthracene* (*in alcohol*). *Max. and log ε at* (2490, 2·49), 2540 (2·74), 2595 (2·86), 2655 (2·84), and 2750 (2·57).

benzylanthracene and the carbinol (XVIII) show typical anthracene spectra, very similar to that of 9 : 10-dimethylanthracene. On the other hand, the photo-oxide of 9-methyl-10-ethoxymethylanthracene and 9 : 10-diethoxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene, show spectra of dihydroanthracene type as expected.

Experimental.

9 : 10-*Dihydroxy*-9 : 10-*dimethyl*-9 : 10-*dihydroanthracene*.—To obtain this diol it is of advantage to prepare the Grignard complex in the presence of anthraquinone, rather than to add the anthraquinone to the preformed alkylmagnesium halide (cf. Guyot and Staehling, *Bull. Soc. chim.*, 1905, **33**, 1144; Bachmann and Chemerda, *J. Org. Chem.*, 1939, **4**, 583; Davies and Kipping, *J.*, 1911, 296). A mixture of anthraquinone (10 g.), magnesium (5 g.), methyl iodide (15 c.c.), benzene (120 c.c.), and ether (60 c.c. was boiled under reflux on the steam bath for 2 hours. The reaction was not unduly vigorous. After cooling, the mixture was decomposed with ice and ammonium chloride. Part of the product separated,

and a further quantity was obtained by evaporation of the ether–benzene layer. The diol (7·2 g.) crystallised from alcohol in colourless prisms, m. p. 185—190°.

9-*Methyl*-10-*methoxymethylanthracene*.—A solution of the above diol (1 g.) and picric acid (2 g.) in methanol (100 c.c.) was boiled under reflux for 2 hours. After concentration and cooling of the mixture, the *picrate* (1·75 g.) separated. Recrystallisation from methanol gave reddish-brown needles, m. p. 124—125° (Found: C, 59·2; H, 4·2. $C_{17}H_{16}O,C_6H_3O_7N_3$ requires C, 59·3; H, 4·1%). Decomposition of the picrate in benzene with dilute alkali gave 9-*methyl*-10-*methoxymethylanthracene* as long pale yellow blades, m. p. 108—109° (from methanol) (Found: C, 86·4; H, 6·7. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%). The same product was obtained when a boiling solution of the diol (0·5 g.) in methanol (20 c.c.) was treated with dilute hydrochloric acid (5 c.c.).

9-*Methyl*-10-*ethoxymethylanthracene*.—Similarly prepared, but recrystallised from ethanol the *picrate* formed small reddish-brown needles, m. p. 117—118° (Found: C, 60·4; H, 4·5. $C_{18}H_{18}O,C_6H_3O_7N_3$ requires C, 60·1; H, 4·4%). Decomposition in the usual way gave 9-*methyl*-10-*ethoxymethylanthracene*, which sublimed without decomposition in a high vacuum and formed pale yellow blades, m. p. 106—107°, from ethanol (Found: C, 86·7; H, 7·1. $C_{18}H_{18}O$ requires C, 86·4; H, 7·3%). The *photo-oxide*, prepared by exposure of a benzene solution of the above product to air and indirect sunlight, formed colourless silky needles, m. p. 153—154° (after sintering), from alcohol (Found: C, 76·9; H, 6·7. $C_{18}H_{18}O_2$ requires C, 76·6; H, 6·4%).

9-*Methyl*-10-*propoxymethylanthracene*.—Similarly prepared, 9-*methyl*-10-*n-propoxymethylanthracene* formed small pale yellow blades or plates, m. p. 101—102°, from methanol (Found: C, 86·5; H, 7·4. $C_{19}H_{20}O$ requires C, 86·3; H, 7·6%). The *picrate* formed reddish-brown needles, which decomposed to an amorphous powder on prolonged drying at 90°. When heated rapidly, it melted indefinitely at *ca.* 120° (Found: C, 61·1; H, 4·5. $C_{19}H_{20}O,C_6H_3O_7N_3$ requires C, 60·8; H, 4·7%).

9-*Methyl*-10-*iodomethylanthracene*.—A mixture of anthraquinone (10 g.), magnesium (5 g.), methyl iodide (15 c.c.), dry benzene (120 c.c.), and dry ether (60 c.c.) was boiled under reflux on the steam-bath for 2 hours. After cooling, the product was gradually added to a solution of hydriodic acid (120 c.c.) and methanol (400 c.c.) at 0°. Acetic acid (400 c.c.) was then added, and the yellow crystalline product (9·5 g.) collected and dried in air. This product, evidently 9-methyl-10-iodomethylanthracene, liberated iodine on attempted recrystallisation, and on heating, and could not be purified for analysis (cf. Sandin and Fieser, *loc. cit.*).

This compound (1 g.) was treated with sodium methoxide (from 2 g. of sodium) in methanol (40 c.c.), and the mixture boiled for 15 minutes. Water was added and the product collected. The resulting solid was extracted with boiling methanol, and the solution filtered from sparingly soluble material (0·2 g.) and treated with excess of picric acid. Decomposition of the resulting picrate (m. p. 120—124°) in the usual way gave 9-methyl-10-methoxymethylanthracene, m. p. 106—107°, not depressed on admixture with a specimen prepared as described above. The insoluble by-product was identified as anthraquinone by m. p. and mixed m. p.

9 : 10-*Dimethylanthracene*.—(i) A solution of the above iodomethyl compound (5 g.) in dioxan (300 c.c.) and concentrated hydrochloric acid (15 c.c.) was added to stannous chloride (50 g.) in dioxan (250 c.c.) and concentrated hydrochloric acid (150 c.c.). The mixture was boiled for 5 minutes and then set aside for 1 hour. Water (2½ l.) was then added. Next morning, the product was collected and recrystallised from benzene–alcohol. A sparingly soluble by-product, 1′ : 2′-*di*-(10-*methylanthranyl*)-*ethane* (0·5 g.), was first obtained. It formed very small colourless prisms, m. p. >300°, from benzene (Found: C, 93·7; H, 6·2. $C_{30}H_{26}$ requires C, 93·6; H, 6·4%). 9 : 10-Dimethylanthracene (2·4 g.) crystallised from benzene in bright yellow prisms, m. p. 179—180°, not depressed on admixture with a specimen prepared by the method of Bachmann and Chemerda (*loc. cit.*).

(ii) A mixture of 9-methyl-10-ethoxymethylanthracene (0·5 g.), acetic acid (8 c.c.) and hydriodic acid (1 c.c.) was boiled for 10 minutes. After cooling, the mixture was diluted with water, and sulphur dioxide was passed into the suspension for a few minutes. The product was collected and recrystallised from benzene. It formed yellow crystals, m. p. 178°, not depressed on admixture with an authentic specimen.

(iii) 9 : 10-Dimethylanthracene (0·25 g.) was also obtained by treatment of the diol (Ia) (0·5 g.) with acetic acid (15 c.c.) and hydriodic acid (2 c.c.), followed by sublimation of the product and recrystallisation from alcohol.

9-*Methyl*-10-*chloromethylanthracene*.—(i) A suspension of 9-methylanthracene (7·5 g.) in glacial acetic acid (45 c.c.) was added to a solution prepared by passing hydrogen chloride into paraformaldehyde (3 g.) suspended in glacial acetic acid. The mixture was kept at 45° for 2 hours and then left at room temperature overnight. After addition of water, the product was collected and recrystallised from benzene. 9-*Methyl*-10-*chloromethylanthracene* (5·5 g.) formed yellow needles, which charred and melted at 192° (Found: C, 80·0; H, 5·5. $C_{15}H_{13}Cl$ requires C, 79·8; H, 5·4%). This compound (1 g.) was boiled with methanol (40 c.c.) and sodium methoxide (from 2 g. of sodium) for 15 minutes. The product, purified by way of the picrate, had m. p. 106—107°, not depressed on admixture with specimens of 9-methyl-10-methoxymethylanthracene prepared by either of the methods described above.

(ii) A stream of hydrogen chloride was passed into a solution of 9-methyl-10-ethoxymethylanthracene (2 g.) in benzene (50 c.c.), for ½ hour. Yellow crystals gradually separated and were collected and added to the material obtained by evaporation of the washed benzene solution. Recrystallisation of the crude material from benzene gave 9-methyl-10-chloromethylanthracene (1·6 g.), identical with that obtained by the first method.

9 : 10-*Dihydroxy*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthracene*.—This diol was prepared by the interaction of benzyl chloride with magnesium in the presence of anthraquinone as described above for the corre-

sponding dimethyl diol. After recrystallisation from alcohol, 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene formed small colourless transparent crystals, m. p. 185°, which became opaque when dried (Found: C, 85·9; H, 6·1. Calc. for $C_{28}H_{24}O_2$: C, 85·7; H, 6·2%). Padova (*Ann. Chim.*, 1910, **19**, 353) gives m. p. 184°.

9 : 10-*Diethoxy*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthracene*.—In an unsuccessful attempt to carry out the anionotropic rearrangement with picric acid, a solution of the above diol (0·5 g.) and picric acid (1 g.) in absolute ethanol was boiled for 1 hour. After cooling, the colourless crystals which had separated were collected and washed free of picric acid. Alcoholic solutions of the crude material had an intense blue fluorescence, showing the presence of traces of rearranged product, but the fluorescence was removed by repeated recrystallisation. 9 : 10-*Diethoxy*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthracene* was obtained as colourless plates, m. p. 248—250° (Found: C, 85·7; H, 7·1. $C_{32}H_{32}O_2$ requires C, 85·7; H, 7·2%).

9-*Formyl*-10-*benzylanthracene*.—A mixture of 9-benzylanthracene (Cook, *J.*, 1926, 2160; 35 g.), methylformanilide (35 g.), phosphorus oxychloride (35 g.), and chlorobenzene (20 c.c.) was heated on a steam-bath for 1½ hours. Crystalline sodium acetate (140 g.), dissolved in water (250 c.c.), was added to the cooled mixture, which was then rapidly steam-distilled. The residue was washed with a little alcohol and recrystallised from acetic acid. 9-*Benzylanthracene*-10-*aldehyde* (30·6 g.) formed bright yellow blades, m. p. 158—160° (Found: C, 89·2; H, 5·55. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%).

9-*Benzyl*-10-α-*hydroxybenzylanthracene*.—A warm benzene solution of 9-formyl-10-benzylanthracene (4 g.) was added to the Grignard solution prepared from bromobenzene (16 c.c.) and magnesium (2·5 g.) in ether. After 2 hours at room temperature, the mixture was decomposed with ice and ammonium chloride. 9-*Benzyl*-10-α-*hydroxybenzylanthracene* (3·2 g.) crystallised from benzene–light petroleum in very small pale yellow prisms, m. p. 170—172° (rapid heating) (Found: C, 89·7; H, 5·9. $C_{28}H_{22}O$ requires C, 89·8; H, 5·9%). The *photo-oxide*, prepared by exposure of a benzene–light petroleum solution of the above compound to air and diffuse sunlight for several days, formed colourless silky needles, m. p. 206—208° (Found: C, 82·8; H, 5·4. $C_{28}H_{22}O_2$ requires C, 82·7; H, 5·5%).

9-*Benzyl*-10-α-*ethoxybenzylanthracene*.—(i) A solution of 9-benzyl-10-α-hydroxybenzylanthracene (1 g.) in absolute ethanol was treated, at room temperature, with 3 drops of concentrated sulphuric acid in a little ethanol. Next morning the crystals which had deposited were collected and recrystallised from alcohol. 9-*Benzyl*-10-α-*ethoxybenzylanthracene* was obtained in almost quantitative yield and formed colourless small plates, m. p. 190—191° (Found: C, 89·5; H, 6·3. $C_{30}H_{24}O$ requires C, 89·5; H, 6·5%.

(ii) A boiling ethanol solution of 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (5 g.) was treated with concentrated hydrochloric acid (5 c.c.), and the mixture boiled for 6 hours. 9-Benzyl-10-α-ethoxybenzylanthracene was obtained in almost quantitative yield and had m. p. 190—191°, alone or mixed with a specimen prepared as described in the first method.

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475. *The Stereochemistry of* 10-*Benzylideneanthrone and* 9-*Benzylidenefluorene.*

By V. M. INGRAM.

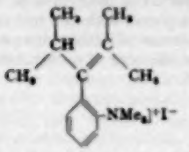
10-*m*-Aminobenzylideneanthrone was expected to show restricted rotation about the single bond between the phenyl group and its side-chain, but it could not be resolved by recrystallisation of its (+)-camphor-10-sulphonate. Optical activity was established by the mutarotation of this salt and by the preparation of an active hydriodide. The *N*-(−)-menthoxyacetyl derivative of the base also resisted resolution, but gave indications of optical activity in its basic portion.

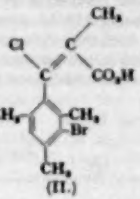
9-*m*-Aminobenzylidenefluorene dibenzoyl-D-tartrate could not be resolved, neither did it mutarotate, but comparison with similar salts of inactive bases gave an indication that the base might be capable of optical activity. The *N*-(−)-menthoxyacetyl derivative proved to be inactive.

MILLS and DAZELEY (*J.*, 1939, 460) and Adams and Miller (*J. Amer. Chem. Soc.*, 1940, **62**, 53) were able to show that arylolefins of the types (I) and (II) exhibited restricted rotation about the single bond joining the phenyl nucleus to the side-chain. In order to ensure sufficient restriction, these compounds possessed either one very large *ortho*-substituent or two smaller ones. The present work was undertaken with the object of increasing the size of the side-chain to such an extent, as in 10-benzylideneanthrone derivatives (III), that there would be restricted rotation with only hydrogen atoms in the *ortho*-positions.

A scale drawing of the essential (lettered) part of (III), constructed by using the usual

interatomic distances and valency angles, indicated that, although carbon atoms *a* and *f* do not interfere, the centres of the hydrogen atoms attached to them overlap by approximately 0·2 A. As a result the benzene ring can no longer lie in the same plane as the 10-methyleneanthrone skeleton, which is itself rigidly planar, and rotation around the single bond C(*d*)—C(*e*) will be effectively restricted. Unsymmetrical substitution in the benzene ring, as in 10-*m*-aminobenzylideneanthrone (III; R = NH_2), will then give rise to an asymmetric molecule which should exist in two optically-active forms.


(I.)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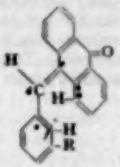
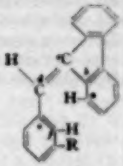

(III.)


(IV.)

10-*m*-Aminobenzylideneanthrone was readily prepared by the reduction of the corresponding nitro-compound with stannous chloride in glacial acetic acid saturated with hydrogen chloride. Attempts to resolve this base by crystallisation of the (+)-camphor-10-sulphonate from alcohol were unsuccessful, as successive crops had identical rotations in pure chloroform, $[M]_D^{20}$ = +98°, +98°. No further attempts at fractionation were made especially as it was found that the base was too weak to form stable salts with optically-active carboxylic acids. The solution of the salt in pure chloroform showed no change in rotation during 10 hours. Addition of alcohol (3·25%) to the chloroform solution produced, however, a change in the value of rotation, and mutarotation which was measured at three temperatures, *viz.* 20·0°, 30·0°, and 35·0° (see Table I and Fig. 1). It is evident that the reaction obeyed a first-order law. From the results it was calculated that the half-life periods were 302, 185, and 127 minutes, respectively, whilst the activation energy for the mutarotation was 10·1 kcals./mol.

This value is one of the lowest recorded for the mutarotation of compounds showing restricted rotation. It is of interest since, according to Kistiakowsky and Smith (*J. Amer. Chem. Soc.*, 1936, **58**, 1043), 20 kcals./mol. is the minimum value required before isolation of the optical isomers can be expected.

TABLE I.

	Salt.	Treatment.	Temp.	$[M_t]_D$.	$[M_\infty]_D$.	10^4k (min.$^{-1}$).	Half-life period, mins.	Remarks.
(1)	10-*m*-Aminobenzylideneanthrone (+)-camphor-10-sulphonate	cryst.	20·0°	+ 98°	—	—	—	*c*, 2·667; no mutarotation
(2)	" "	"	20·0	+135°	+72°	23	302	energy of activation = 10·1 kcals.
(3)	" "	"	30·0	+133	+50	38	185	
(4)	" "	"	35·0	+132	+44	55	127	
(5)	" "	synthesised in soln.	30·0	+125	+50	32	219	different batch of solvent
(6)	" "	synthesised in soln.; boiled	30·0	− 55	+50	32	219	
(7)	Pyridine (+)-camphor-10-sulphonate	synthesised in soln.	30·0	+128	—	—	—	
(8)	10-*m*-Aminobenzylideneanthrone hydriodide	see text	20·0	−187	0	12	600	

Solvents: pure chloroform in (1), pure chloroform containing 3·25% of alcohol (added immediately before the observations were commenced) in all others.
Concentration: *c*, 4·164 in (2)—(6); equimolecular concentrations in (7) and (8).

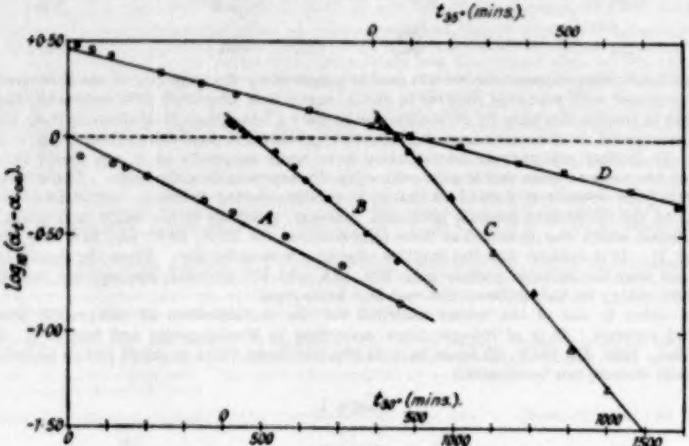
From the experimental results recorded in Table I it will be noticed that the initial rotation of 10-*m*-aminobenzylideneanthrone (+)-camphor-10-sulphonate at 30° $[M_t]_D^{30}$ = +133°, lies remarkably close to the rotation of pyridine (+)-camphor-10-sulphonate in the same solvent, $[M]_D^{30}$ = +128°, the difference between these two values being very small compared with the change in rotation which occurs during the mutarotation, $[M]_D^{30}$ = +133° ⟶ +50°. The conclusion was therefore drawn that the basic portion of the molecule makes no contribution

to the initial rotation and that the crystalline salt consists of a mixture, or perhaps a compound, of the two salts (+)-base(+)-acid and (−)-base(+)-acid, in molecular proportions.

A solution prepared from equimolecular amounts of the (±)-base and (+)-camphor-10-sulphonic acid in chloroform containing alcohol (3·25%) had an initial rotation of $[M_0]_D^{20°} = +125°$ and then mutarotated to the same equilibrium value $[M_\infty]_D^{20°} = +50°$, as that found for the crystallised salt (see Table I and Fig. 2). The initial value is very close to that of the original crystallised salt, which therefore contains equal amounts of the (+)- and (−)-bases.

The mutarotation of the "synthetic" salt proceeded at a slower rate than that of the original crystallised salt, the half-life period being 219 minutes as compared with 185 minutes, but this lower speed is probably due to the fact that different specimens of chloroform were employed in the two experiments. It had been found previously that the rate of mutarotation was dependent on the manner in which the solvent had been purified.

FIG. 1.



A, B, C: (±)-10-m-*Aminobenzylideneanthrone* (+)-*camphor*-10-*sulphonate* at 20°, at 30°, at 35°.
D *Activated* 10-m-*aminobenzylideneanthrone hydriodide*.

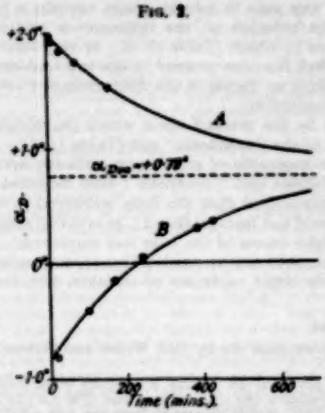
From the values of $[M_\infty]_D$ at 20° and 35° given in Table I it will be observed that the positive rotation of the equilibrium mixture diminishes rapidly with rise of temperature, indicating a displacement of the equilibrium in favour of the salt derived from the (−)-base. At the temperature of boiling chloroform the displacement occurs to such an extent that the equilibrium mixture shows actually a negative rotation. Thus a chloroform solution of the "synthetic" salt, prepared as described previously, after being heated to boiling and rapidly cooled to 30° had an initial rotation of $[M_0]_D^{30°} = -55°$ which changed at the same rate as before to the same final value (see Table I and Fig. 2). Since there is no reason to suppose that −55° represents the maximum rotation of the optically pure (−)-base(+)-acid salt, the base must have a molecular rotation greater than ±180°.

Final confirmation of the optical activity of 10-*m*-aminobenzylideneanthrone was obtained by the preparation of a lævorotatory hydriodide. A solution of the "synthetic" (+)-camphor-10-sulphonate in chloroform containing 3·25% alcohol was heated to boiling, cooled rapidly to 20°, and then vigorously shaken with concentrated aqueous potassium iodide. The hydriodide remaining in the chloroform solution had an initial rotation of −187°, and then underwent mutarotation with a half-life period of 600 minutes, obeying a first-order law (see Fig. 1). The progressive darkening of the solution prevented direct observation of the final

zero reading, but the actual observations agreed very well with the values calculated by the method of least squares on the assumption of a final zero reading.

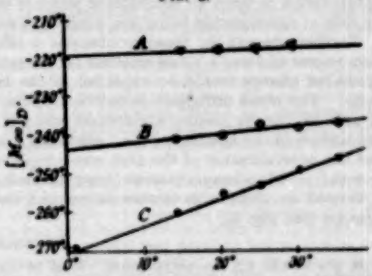
10-*m*-[(−)-Menthoxyacetamido]benzylideneanthrone, prepared from (−)-menthoxyacetyl chloride, could not be resolved by crystallisation from alcohol and ethyl acetate, the first and the second crop having almost identical rotations, *viz.* $[M]_D^{20}$ = −255° and −254° in chloroform, respectively. The rotations remained constant during 2½ hours and showed no change even after the addition of alcohol, glacial acetic acid, or alcoholic hydrogen chloride to the chloroform solution; heating in methyl salicylate to 150° for one hour also produced no change. On the other hand the rotation in chloroform solution showed a marked increase with rise of temperature compared with that of (−)-menthoxyacetanilide (see Fig. 3). This increase may of course be the ordinary variation of rotatory power with temperature, but it could also be connected with the existence of the benzylideneanthrone part of the molecule in optically active forms. The two diastereoisomeric menthoxyacetyl derivatives [(−)-acyl(−)amine and (−)-acyl(+)-amine)] may racemise too rapidly to permit of the mutarotation being followed by direct polarimetric observation, but would form equilibrium mixtures of varying composition at different temperatures; this variation in composition may manifest itself by a marked change in the equilibrium values of the rotation with rise of temperature.

FIG. 2.



A "*Synthetic*" 10-m-*aminobenzylideneanthrone* (+)-*camphor*-10-*sulphonate*.
B *Boiled* 10-m-*aminobenzylideneanthrone* (+)-*camphor*-10-*sulphonate*.

FIG. 3.



A 9-m-[(−)-*Menthoxyacetamido*]*benzylidenefluorene*.
B (−)-*Menthoxyacetanilide*.
C 10-m-[(−)-*Menthoxyacetamido*]*benzylideneanthrone*.

The carbon skeleton *a*—*f* in 9-benzylidenefluorene (IV; R = H) is very similar to that present in 10-benzylideneanthrone, but the replacement of the 6-membered *centre* anthrone ring by a 5-membered ring in fluorene must result in a considerable increase in the distance between carbon atoms *a* and *f*. Nevertheless it was expected that restricted rotation would occur, though the optical stability of the molecule should be less than in the case of its anthrone analogue.

9-*m*-Nitrobenzylidenefluorene (IV; R = NO_2) was prepared by a method similar to that used by Thiele and Henle (*Annalen*, 1906, **347**, 296) for the preparation of 9-benzylidenefluorene. Reduction with stannous chloride in ether saturated with hydrogen chloride furnished the amine hydrochloride (IV; R = NH_2,HCl). The free base could not be obtained crystalline. The (+)-camphor-10-sulphonate of this base was unsuitable for optical examination because of its very sparing solubility in neutral organic solvents. The more soluble dibenzoyl-D-tartrate could not be resolved by crystallisation from alcohol, successive fractions having almost identical rotations $[M]_D^{20}$ = −353°, −349°. As there was also no evidence of mutarotation, the molecular rotation of this salt was compared, under identical conditions, with the rotations of dibenzoyl-D-tartrates of the inactive bases, pyridine, 1-naphthylamine, and 9-*m*-aminobenzylfluorene (see Table II). The rotation given in (4) refers to the crystallised salt of the

fluorene base, whilst the values in (5) and (6) were obtained from solutions of the salt prepared directly from the base and the acid immediately before optical examination.

TABLE II.

Base.	Molar ratio, base : acid.	$[M]_D^{20}$.
(1) Pyridine	2 : 1	−420°
(2) 1-Naphthylamine	2 : 1	−417
(3) 9-*m*-Aminobenzylfluorene	2 : 1	−418
(4) 9-*m*-Aminobenzylidenefluorene (cryst. salt)	2 : 1	−354
(5) " " (synth. salt)	2 : 1	−345
(6) " " "	4 : 1	−259

Solvent: pure chloroform containing 3·25% of alcohol. *c*, 0·726 in (4), corresponding molarities in the others.

It will be observed that whereas the rotations of the salts of the inactive bases lie within ±2°, or 0·5% of their mean value −419°, the rotation of 9-*m*-aminobenzylidenefluorene dibenzoyl-D-tartrate differs by as much as 65°, or 15%. This difference would appear to indicate that there is a contribution by the base to the total rotatory power of the salt, a conclusion which implies that 9-*m*-aminobenzylidenefluorene might be capable of existing in optically-active modifications and that the salt, at any rate in solution, may contain a preponderance of the dextrorotatory form. Since the rotation of the dibenzoyl-D tartrate, " synthesised " in solution from the acid and the free (±)-base [Table II (5)], is very near in value to that of the crystallised salt (4), it follows that the base present in the salt undergoes mutarotation to form an equilibrium mixture containing an excess of the dextrorotatory form, the rate of racemisation being too rapid for visual observation.

Further support for these conclusions is afforded by the marked effect which the addition of an excess of free (±)-base exercise on the rotation of the " synthetic " salt [Table II (6)]; no significant change would be expected, if the base is incapable of existing in optically-active forms. The small difference in rotation of the crystallised and " synthetic " salts recorded in (4) and (5) can be readily understood when it is remembered that the base employed in the preparation of the solution of the " synthetic " salt could not be crystallised; in order to ensure that the neutralisation of the acid was complete a slight excess of the base was employed.

9-*m*-[(−)-Menthoxyacetamido]benzylidenefluorene could not be resolved by crystallisation. It showed no observable mutarotation and only very slight variation of rotation with temperature (see Fig. 3).

EXPERIMENTAL.

M. p.s and b. p.s are uncorrected. Most of the microanalyses are by Drs. Weiler and Strauss of Oxford.

10-m-*Nitrobenzylideneanthrone*.—This compound was prepared by boiling a mixture of anthrone (90 g.), *m*-nitrobenzaldehyde (75 g.), piperidine (7 c.c.), pyridine (80 c.c.), and xylene (190 c.c.) in an atmosphere of coal gas for 6 hours. The product (82 g., 55%) which separated from the cool solution was washed with cold acetone and then with the same solvent containing a little hydrochloric acid, and finally crystallised from acetic acid; it formed small canary-yellow prisms which exhibited pronounced thermochromism and had m. p. 174·5—175·5° (Found: C, 77·3; H, 4·0; N, 4·2. Calc. for $C_{21}H_{13}O_3N$: C, 77·1; H, 4·0; N, 4·3%). Padova (*Ann. Chim. Phys.*, 1910 (8), **19**, 386; *Compt. rend.*, 1905, **141**, 681) gives m. p. 165·5—166·5°.

10-m-*Aminobenzylideneanthrone*.—Dry hydrogen chloride was passed into a suspension of powdered, fused stannous chloride (105 g.) in glacial acetic acid (550 c.c.) until solution was effected. On the addition of 10-*m*-nitrobenzylideneanthrone (50 g.), dissolved in boiling acetic acid (450 c.c.), 10-*m*-aminobenzylideneanthrone stannichloride was rapidly deposited in slender, crimson needles which after being successively washed with acetic acid and alcohol, were suspended in the latter solvent (500 c.c.) and warmed with aqueous ammonia (70 c.c.; 0·88). The solid was separated, digested with cold aqueous sodium hydroxide (300 c.c.; 4*N*.) in order to remove stannic hydroxide, washed with water, and combined with the product obtained by precipitating the alcoholic mother-liquor with water. The solids were dried azeotropically in toluene solution (200 c.c.) by using a Dean and Stark water separator. The hot solution was decanted from the residual tin compounds and ammonium chloride which were again extracted with toluene (50 c.c.). The combined toluene extracts, after clarification with charcoal, deposited 10-m-*aminobenzylideneanthrone* in soft yellow needles (30 g., 66%) which had m. p. 172—173° (sintering at 157°) and showed no signs of thermochromism (Found: C, 84·2; H, 5·0; N, 4·6. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·1; N, 4·7%).

The (+)-*camphor*-10-*sulphonate* was prepared from equivalent quantities of the base (6·0 g.) and the acid (4·6 g.) in boiling alcohol (120 c.c.), and separated in rosettes of soft yellow needles (7·0 g.), m. p. 190·5—192·5°, $[M]_D^{20}$ +98° in pure chloroform (α_D^{20} = + 0·99°, *l* = 2, *c* = 2·667) (Found: C, 69·8; H, 5·9; N, 2·6. $C_{31}H_{31}O_4NS$ requires C, 70·3; H, 5·9; N, 2·6%). The mother-liquor furnished a second crop of the salt (0·9 g.) having the same rotatory power in pure chloroform, $[M]_D^{20}$ = + 98° (α_D^{20} = + 0·78°, *l* = 2, *c* = 2·105). Neither of the crops showed any change in rotation during 10 hours.

Mutarotation of (±)-10-m-*Aminobenzylideneanthrone* (+)*Camphor*-10-*sulphonate.*—The chloroform employed in the following experiments was purified by freeing it from alcohol by prolonged washing with running water, followed by azeotropic drying. The dry chloroform was finally fractionally distilled through a 2-ft. column packed with glass helices; it usually boiled over a range of ±0·1°, and did not develop any acidity when kept in the dark for several months.

All polarimetric determinations were made in jacketed 2-dm. tubes maintained within ±0·1° of the stated temperature; the sodium-D line was used. Solutions in chloroform–alcohol were prepared by dissolving the compound for examination in chloroform and adding the absolute alcohol immediately before commencing the observations. The solutions were made up at the same temperature as that at which the determinations were carried out.

The values of k and the half-life period (see Table I) were determined from the best straight line (see Fig. 1) calculated by the method of least squares from the plot of $\log_{10}(\alpha_t - \alpha_\infty)$ against the time, t. From the values of k obtained at the three temperatures the energy of activation for the mutarotation of (±)-10-m-aminobenzylideneanthrone (+)-camphor-10-sulphonate in chloroform containing 3·25% of alcohol was found to be 10·1 kcals./mol.

Rotation of Pyridine (+)-*Camphor*-10-*sulphonate.*—A solution of this salt was examined at 30·0° under the same conditions and at the same molar concentration as in the previous experiments; it showed no change in rotation during 12 hours.

Mutarotation of "Synthetic" (±)-10-m-*Aminobenzylideneanthrone* (±)-*Camphor*-10-*sulphonate.*—The solution became too dark for further observation after 154 minutes.

A second solution of the same "synthetic" salt, having the same concentration, was heated under reflux on the steam-bath for 2 hours, cooled rapidly to 30°, and then examined polarimetrically at the same temperature. The solution became too dark for readings to be taken after 425 minutes.

Note: The sample of chloroform used in these and the following experiment was from a different batch from that previously employed. Although both batches had apparently had the same treatment in purification, it had been noticed that the rate of mutarotation is extremely sensitive to minute traces of impurities, and it has been impossible to obtain two batches of chloroform with the same characteristics.

Optically-active 10-m-*Aminobenzylideneanthrone Hydriodide.*—A solution of "synthetic" (±)base-(+)-camphor-10-sulphonate in chloroform containing 3·25% of alcohol was boiled under reflux for 2 hours, then rapidly cooled to 15° and shaken vigorously for two minutes with an aqueous solution of potassium iodide (20 g. in 20 c.c.). The chloroform solution was separated, filtered, and then examined polarimetrically at 20·0°. For the calculation the time at which the shaking with potassium iodide commenced was taken as the zero time of the mutarotation. The solution became too dark after 1585 minutes.

10-m-[(−)-*Menthoxyacetamido*]*benzylideneanthrone.*—A solution of (−)-menthoxyacetyl chloride (11·5 g.) in anhydrous ether (50 c.c.) was added slowly during 20 minutes to a boiling suspension of 10-*m*-aminobenzylideneanthrone (15·0 g.) in the same solvent (50 c.c.) containing slightly more than the equivalent amount of pyridine (5 c.c.). The mixture was then heated under reflux for 1½ hours, the solid being occasionally broken up during this period. The precipitated pyridine hydrochloride was removed from the cold reaction mixture and washed several times with ether. The ethereal solution was washed successively with dilute hydrochloric acid and water and furnished 10-m-[(−)-*menthoxyacetamido*]*benzylideneanthrone* in pale-yellow needles (22·5 g., 90%), which crystallised from ethyl acetate and had m. p. 124·5° and $[M]_D^{20} = -235°$ in chloroform ($\alpha_D^{20} = -7·04°$, $l = 2$, $c = 6·81$) (Found: C, 80·2; H, 7·2. $C_{32}H_{33}O_3N$ requires C, 80·3; H, 7·2%).

Concentration of the ethyl acetate mother-liquor yielded a second crop (1·5 g.), m. p. 123—124°, $[M]_D^{20} = -254°$ in chloroform ($\alpha_D^{20} = -7·06°$, $l = 2$, $c = 6·84$).

In chloroform containing 1% of alcohol the observed rotation, $[M]_D^{20} = -242°$, did not change during 6 hours. On the addition of 0·1 c.c. of a 4% alcoholic solution of concentrated hydrochloric acid to the chloroform solution (20·2 c.c.) there was no significant change during 15 hours. In chloroform containing 3·25% of alcohol the molecular rotation of −240° at 30° remained constant over 24 hours and also after addition of 0·1 c.c. of glacial acetic acid to the solution (20·65 c.c.). In methyl salicylate it gave $[M]_D^{20} = -291°$, and this value remained constant when the solution was heated for one hour at 100° and later for one hour at 150°.

Comparison of the Rotations of 10-m-[(−)-*Menthoxyacetamido*]*benzylideneanthrone and* (−)-*Menthoxyacetanilide.*—A solution of the benzylideneanthrone derivative in chloroform ($c = 6·84$ at 14°) was examined at temperatures between 14° and 35°; its rotation was also measured at 1°.

A solution of (−)-menthoxyacetanilide of the same molar concentration was examined under the same conditions. This solution was prepared by adding freshly distilled aniline (1·301 g., 2 mols.) to (−)-menthoxyacetyl chloride (1·613 g.) dissolved in chloroform. A white crystalline precipitate of aniline hydrochloride separated immediately and the reaction was completed by gentle boiling for one hour. The mixture was cooled and made up to 50·0 c.c. with chloroform and before examination was strained through cotton wool. The results are given in Fig. 3; the expansion of the solution has been taken into account.

9-m-*Nitrobenzylidenefluorene.*—Warm alcoholic solutions of sodium (30 g. in 500 c.c.) and *m*-nitrobenzaldehyde (130 g. in 300 c.c.) in absolute alcohol were added successively to a hot solution of technical fluorene (100 g.) in the same solvent (2 l.). The solution became very dark and, when kept overnight, deposited a brown crystalline solid which, after being washed with alcohol and then with dilute hydrochloric acid, was dissolved in ethyl acetate (600 c.c.) and allowed to percolate through a

12-in. column of activated alumina. Concentration of the red percolate to 200 c.c. furnished 9-m-*nitrobenzylidenefluorene* (44 g., 24·5%) which, after crystallisation from alcohol containing ethyl acetate (10%), had m. p. 115—115·5° and showed no signs of thermochromism (Found: C, 80·2; H, 4·5; N, 4·7. $C_{20}H_{13}O_2N$ requires C, 80·3; H, 4·4; N, 4·7%).

9-m-*Aminobenzylidenefluorene*.—Dry hydrogen chloride was passed into a well-stirred suspension of finely powdered, fused stannous chloride (100 g.) in anhydrous ether (1250 c.c.) until the solid had disappeared and a lower viscid layer had separated out. After the portionwise addition of 9-*m*-nitrobenzylidenefluorene (44 g.) the mixture was stirred for a further 5 hours whereupon 9-*m*-aminobenzylidenefluorene stannichloride separated as a buff-coloured solid in theoretical yield (68 g.). A solution of the stannichloride in hot alcohol (200 c.c.) deposited, on cooling, very pale-yellow needles of 9-m-*aminobenzylidenefluorene hydrochloride* (22 g., 49%) which after further crystallisation from alcohol had m. p. 229—230°. A second crop (18·5 g.; total yield 90%) of the hydrochloride was obtained by adding aqueous ammonia (80 c.c.; *d* 0·88) to the alcoholic mother-liquor, filtering from the stannic hydroxide thus precipitated, and pouring into dilute hydrochloric acid (4·1.; 2N.) (Found: C, 78·3; H, 5·6; N, 4·3. $C_{20}H_{16}NCl$ requires C, 78·6; H, 5·3; N, 4·6%. Found: 1·00 g. neutralised 32·2 c.c. of 0·1N-sodium hydroxide. 1·00 g. of $C_{20}H_{15}N,HCl$ requires 32·7 c.c. of 0·1N-sodium hydroxide).

The free base was obtained as an amorphous yellow solid by stirring the finely powdered hydrochloride (1·0 g.) with dilute aqueous ammonia (5 c.c. of *d* 0·88 solution in 200 c.c. of water). All attempts to obtain the base crystalline were unsuccessful. It decomposes when kept, and was therefore always freshly prepared.

9-m-*Aminobenzylidenefluorene* (+)-*Camphor*-10-*sulphonate*.—This salt was prepared by heating the hydrochloride (9·67 g.) and silver (+)-camphor-10-sulphonate (10·68 g.) in boiling absolute alcohol (400 c.c.). After one hour the solution still contained a slight amount of silver, which was removed by heating it for a further 15 minutes with a few crystals of the amine hydrochloride. The solution was filtered from silver chloride and when cooled deposited the (+)-*camphor*-10-*sulphonate* in pale-yellow needles (11·0 g.) which had m. p. 214—215° and were readily soluble in pyridine and quinoline, but only very sparingly soluble in neutral organic solvents [Found: C, 71·8; H, 6·4; N, 2·8%; *M* (Rast), 414. $C_{30}H_{31}O_4NS$ requires C, 70·2; H, 6·2; N, 2·8%; *M*, 501]. The salt had $[M]_D^{20}$ +80° in quinoline (α_D^{20} +1·60°, *l* = 2, *c* = 5·00) and $[M]_D^{20}$ +124° in chloroform containing 9% by volume of pyridine (α_D^{20} +4·46°, *l* = 2, *c* = 9·00); neither solution showed mutarotation.

9-m-*Aminobenzylidenefluorene Dibenzoyl*-D-*tartrate*.—A solution of the base (5·0 g., 0·02 mol.) and the acid (4·2 g., 0·01 mol.) (containing 1·5 mols. of water of crystallisation) in the minimum amount of boiling alcohol (25 c.c.) deposited, on cooling, the *dibenzoyl*-D-*tartrate* in microscopic, pale-orange needles, m. p. 140°, $[M]_D^{20}$ −354° in chloroform containing 3·25% of alcohol (α_D^{20} −1·15°, *l* = 4, *c* = 0·86) (Found: C, 77·4; H, 5·0. $C_{44}H_{43}O_8N_2$ requires C, 77·7; H, 5·0%). Concentration of the original mother-liquor furnished a further crop having almost the same rotation, $[M]_D^{20}$ −349° in chloroform containing 3·25% alcohol (α_D^{20} −0·39°, *l* = 2, *c* = 0·50).

Comparison of Rotations of Several Dibenzoyl-D-*tartrates*.—The rotations of the dibenzoyl-D-tartrates of 1-naphthylamine, pyridine, and 9-*m*-aminobenzylfluorene were compared with the rotations of crystallised and "synthetic" 9-*m*-aminobenzylidenefluorene dibenzoyl-D-tartrate (see Table II). In all cases the solutions were prepared by suspending the salt, or the equivalent quantities of the base and acid, in chloroform (40·0 c.c.) and adding absolute alcohol (1·3 c.c.). The concentration of dibenzoyl-D-tartaric acid was the same in all cases and corresponded to 0·29 g. of the anhydrous acid in 100 c.c. of solution.

9-m-[(−)-*Menthoxyacetamido*]*benzylidenefluorene*.—A suspension of 9-*m*-aminobenzylidenefluorene hydrochloride (15·5 g.) in anhydrous ether (50 c.c.), containing pyridine (10 c.c.), was heated to boiling for ½ hour and a solution of (−)-menthoxyacetyl chloride (11·5 g.) in ether (50 c.c.) was then slowly added. After being heated for a further 2½ hours, the ethereal solution was filtered and washed successively with dilute hydrochloric acid, water, aqueous sodium hydroxide, and water again; it was then dried (Na_2SO_4), and the solvent was removed. The residual syrup could not be crystallised, but after exposure to the laboratory atmosphere for several months it partially solidified. Trituration with light petroleum (b. p. 40—60°) containing a little ether furnished 6·0 g. of 9-m-[(−)-*menthoxyacetamido*]-*benzylidenefluorene*, which on crystallisation from the same solvent separated as a tangled mass of long, slender needles, m. p. 79—80°, $[M]_D^{20}$ −220° in chloroform (α_D^{20} −4·19°, *l* = 2, *c* = 4·48); there was no evidence of mutarotation. The rotations at different temperatures, in pure chloroform, are recorded in Fig. 3; the values given have been corrected for the expansion of the solution.

Addition of light petroleum (b. p. 40—60°) to the mother-liquor furnished a second crop of the (−)-menthoxyacetyl derivative having m. p. 80—82° and $[M]_D^{20}$ −217° in chloroform (α_D^{20} −4·13°, *l* = 2, *c* = 4·48) (Found: C, 81·9; H, 7·9. $C_{32}H_{41}O_2N$ requires C, 82·5; H, 7·6%).

9-m-*Aminobenzylfluorene*.—9-*m*-Nitrobenzylidenefluorene (2·0 g.) dissolved in ethyl acetate (75 c.c.) was stirred vigorously in hydrogen at atmospheric pressure with palladised charcoal (0·5 g.; 14%). The reduction, at 42°, was complete in 3 hours. After filtration from the catalyst, the solution was evaporated and furnished 9-m-*aminobenzylfluorene* as a pale-yellow oil which slowly solidified (1·8 g., 99%), and then crystallised from alcohol (15 c.c.) in short cream-coloured prisms, m. p. 105·5—106·5° (Found: C, 87·6; H, 6·4; N, 5·5. $C_{20}H_{17}N$ requires C, 88·5; H, 6·3; N, 5·2%).

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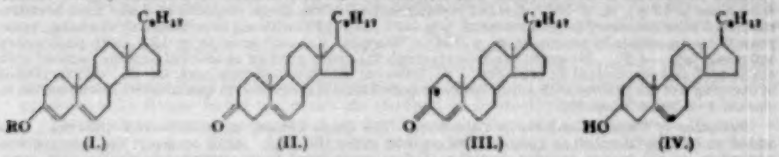
476. *A Conversion of Cholest-4-en-3-one into Cholesterol.*

By Arthur J. Birch.

The enol-acetate (I; R = Ac) of cholest-4-en-3-one (III) reacts with potassium amide in liquid ammonia, followed by water, to give chiefly cholest-5-en-3-one (II).

The equilibrium between a βγ- and the corresponding αβ-unsaturated ketone, *e.g.*, cholest-5-en-3-one (II) and cholest-4-en-3-one (III), is rapidly established in the presence of acidic or alkaline catalysts, and is usually greatly in favour of the αβ-unsaturated isomer. The conversion of the αβ- into the βγ-isomer can then be accomplished only by indirect means. Cholest-4-en-3-one



(I.) (II.) (III.) (IV.)

(III) has been converted into cholesterol (IV) by Reich and Lardon (*Helv. Chim. Acta*, 1946, **29**, 671),* but the process is rather laborious. A desirable step in such a conversion would be the direct preparation of the unconjugated ketone (II) from the conjugated ketone (III).

It has been pointed out (Birch, *J.*, 1950, 1551) that a mesomeric anion of the type (V) may be expected to add a proton to give a high proportion of the unconjugated ketone (VI)

if the addition takes place under conditions where it is irreversible. This expectation depends on the fact that the product is then determined by a reaction rate rather than by an equilibrium position. In effect, the high energy of the anion is used in part to convert the conjugated isomer into the unconjugated isomer of higher energy level. The conditions are fulfilled when the proton source is a much stronger acid than the ketone formed (pK about 20), but not acidic enough to bring about the acid-catalysed equilibrium. Water is therefore a suitable proton-donor, and to it can be added a weak acid like ammonium chloride to remove the alkali formed in the reaction.

If the conjugated ketone is to be used as the source of the anion, it must enolise in such a way as to provide eventually the oxygen atom at the end of the charged system. There appeared to be some possibility that cholest-4-en-3-one would provide the desired salt (I; R = K), since the enol-acetate is known to be 3-acetoxycholesta-3 : 5-diene (I; R = Ac) (Westphal, *Ber.*, 1937, **70**, 2128; Inhoffen, *Ber.*, 1936, **69**, 2144). However, some experiments kindly carried out by Dr. S. Sunner showed that the starting ketone (III) was recovered after treatment with potassium amide in liquid ammonia, followed by water. Under these conditions enolisation therefore proceeds most rapidly by the loss of a proton from the 2-position. The desired enolate (I; R = K) was eventually obtained from 3-acetoxycholesta-3 : 5-diene (I; R = Ac) by the action of potassium amide in ammonia, and gave rise as expected to cholest-5-en-3-one (II).

While this work was in progress it was reported by Shoppee and Summers (*J.*, 1950, 687) that cholest-5-en-3-one (II) is reduced by lithium aluminium hydride to yield principally cholesterol (IV). This work has been confirmed on the ketone obtained by the present method. The isomerisation and reduction reactions in conjunction thus make possible the introduction into the steroid ring B of the 5-double bond characteristic of cholesterol and many other sterols, together with the production of the 3-hydroxyl group in the natural steric configuration. The 4-unsaturated ketones can be obtained from the saturated ketones having the ring junction A–B in either the *cis*- or the *trans*-configuration (Rosenkranz, Kaufman, Pataki, and Djerassi, *J. Amer. Chem. Soc.*, 1950, **72**, 1046).

An immediate application of the reactions would be the preparation of radioactive cholesterol from radioactive cholestenone (Turner, *J. Amer. Chem. Soc.*, 1950, **72**, 579).

* [*Added, June 18th*, 1950.] After this paper had been submitted for publication, Dauben and Eastham (*J. Amer. Chem. Soc.*, 1950, **72**, 2305) described the direct production of cholesterol by reduction of the enol-acetate of cholestenone. This process probably follows the route here described, without the isolation of the intermediate βγ-unsaturated ketone.

Experimental.

Cholest-5-en-3-one from Cholest-4-en-3-one.—3-Acetoxycholesta-3 : 5-diene (Westphal, *loc. cit.*) (1·20 g.) was dissolved in pure ether (10 c.c.) and stirred into potassium amide (from the metal, 1·0 g.) in liquid ammonia (100 c.c.). After 1 hour, the suspension was poured cautiously into a solution of ammonium chloride (10 g.) in water (150 c.c.). The product was extracted as rapidly as possible with 4 successive portions of ether (50 c.c.), the combined extract washed 3 times with water (100 c.c.), a small piece of solid carbon dioxide added to neutralise any remaining ammonia, and the solution again washed with water and dried (Na_2SO_4). The residue left by evaporation of the ether was crystallised from methanol–acetone (1 : 1). The crude cholest-5-en-3-one so obtained formed colourless needles (0·6 g.), m. p. 110—115°. The gummy substance in the mother-liquor seemed to consist principally of a mixture of cholest-4- and -5-en-3-one, because passage through a column of alumina in benzene solution (conditions known to cause isomerisation of the latter ketone to the former) gave cholest-4-en-3-one (0·19 g.), m. p. 80°. Several crystallisations of the crude cholest-5-en-3-one from acetone–methanol were necessary to give material, $[\alpha]_D$ −2°, m. p. 125° with slight preliminary sintering, undepressed by an authentic specimen, m. p. 126°. Westphal (*loc. cit.*) gives m. p. 127°, with preliminary softening, $[\alpha]_D$ −4·2°. Attempts to chromatograph the crude product on neutral alumina (washed with acetic acid and reactivated at 280—300°; cf., however, Shoppee and Summers, *loc. cit.*, who succeeded in carrying out the process with a differently prepared alumina) resulted in quantitative isomerisation to cholest-4-en-3-one, m. p. 80°.

Reduction of Cholest-5-en-3-one to Cholesterol.—The crude ketone, m. p. 110—115° (200 mg.), was added to lithium aluminium hydride (100 mg.) in ether (10 c.c.). After an hour, the mixture was worked up in the known manner, and the product crystallised from methanol as needles (150 mg.), m. p. 135—140°. Two more crystallisations from methanol gave pure cholesterol as flat needles, m. p. 148°, undepressed by an authentic specimen. It was further identified by formation of the acetate, m. p. 115°, undepressed by an authentic specimen, and of a precipitate with alcoholic digitonin.

This work was carried out during the tenure of the Smithson Research Fellowship of the Royal Society. The author is grateful to the Nuffield Research Foundation for financial assistance, to Professor A. R. Todd, F.R.S., for the hospitality of his laboratory, and to Dr. S. Sunner for assistance in the preliminary stages of the work.

The University Chemical Laboratory, Cambridge. [*Received, May 17th*, 1950.]

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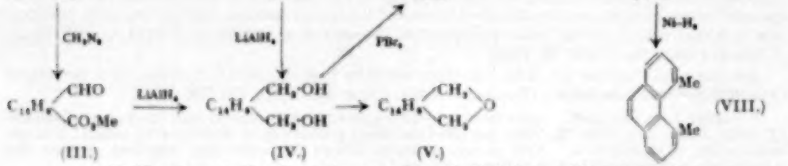
477. *The Synthesis of 4 : 5-Dimethylphenanthrene.*

By G. M. Badger, (Miss) J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott.

A series of convenient reactions for the preparation, from pyrene, of 4 : 5-dimethylphenanthrene and some of its derivatives is described. Ultra-violet absorption data for the hydrocarbon indicate the absence of any marked steric inhibition of resonance.

Phenanthrene derivatives with methyl substituents in the 4- and the 5-position are of considerable interest from the point of view of the nature of the steric hindrance associated with such a structure (Cook, *Ann. Reports*, 1942, **39**, 172; cf. Cook and Kennaway, *Amer. J. Cancer*, 1938, **33**, 55; Newman *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 2295; 1947, **69**, 3023; 1948, **70**, 1913; Campbell, Ph.D. Thesis, Glasgow, 1949). Unsuccessful attempts to synthesise the parent hydrocarbon, 4 : 5-dimethylphenanthrene, have been reported by Haworth and Sheldrick (*J.*, 1934, 1950; cf. *ibid.*, p. 456) and by Lewis and Elderfield (*J. Org. Chem.*, 1940, **5**, 290). The ready preparation of 4-formyl phenanthrene-5-carboxylic acid (I) by the ozonisation of pyrene (Vollmann *et al.*, *Annalen*, 1937, **531**, 1; Fieser and Novello, *J. Amer. Chem. Soc.*, 1940, **62**, 1855) suggested the following route for its synthesis; this has been accomplished and the yield at every stage was of the order of 80%.



($C_{14}H_8$ represents the phenanthrene nucleus substituted at positions 4 and 5.)

The aldehydo-acid was found not to give derivatives with carbonyl reagents; its constitution is therefore best represented by the lactol structure (I). Esterification of the acid with methanolic hydrogen chloride gave the corresponding ϕ-ester (II), which likewise gave no carbonyl derivatives. Treatment of the acid with diazomethane, however, furnished an isomeric methyl ester, which, as it readily gave a 2 : 4-dinitrophenylhydrazone, almost certainly possessed the structure (III). Reduction of either of these methyl esters with lithium aluminium hydride (cf. *inter al.*, Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197) furnished 4 : 5-bishydroxymethylphenanthrene (IV) in excellent yield. The action of hydrogen chloride on this diol did not furnish the expected bischloromethyl compound, the only product formed being the cyclic ether (V). The corresponding bisbromomethyl compound (VI), however, was found to be readily obtainable by the action of phosphorus tribromide on the diol. Attempts to reduce (VI) directly to 4 : 5-dimethylphenanthrene were surprisingly unsuccessful; catalytic hydrogenation and lithium aluminium hydride reduction both gave the cyclic ether (V) as the sole isolable product. The bisbromomethyl compound was therefore treated with thiourea to give a quantitative yield of the di*iso*thiuronium dibromide (VII) which underwent smooth hydrogenolysis with Raney nickel to furnish the required 4 : 5-dimethylphenanthrene.

This work was nearing completion at the time of publication of the paper by Newman and Whitehouse (*J. Amer. Chem. Soc.*, 1949, **71**, 3664) who prepared 4 : 5-dimethylphenanthrene in 17% yield by fission of the cyclic ether (V) with phosphorus and hydriodic acid at 165° for 17 hours. The smooth low-temperature reactions used in the present work are preferable to this drastic procedure with the risk of molecular rearrangement. The physical constants of our hydrocarbon and its derivatives agreed well with the corresponding data of the American workers.

The ultra-violet absorption data (in ethanol) for the 4 : 5-substituted phenanthrenes were kindly determined by Dr. E. A. Braude and the results are tabulated below.

Compound.	$\lambda_{max.}$, A.	ε.	Compound.	$\lambda_{max.}$, A.	ε.	Compound.	$\lambda_{max.}$, A.	ε.
(I)	2510	34,000	(IV)	2580	55,000	(III)	2720	25,000
	2580	34,000		2920	9,000		2800	24,000
	2650	34,000		3010	11,000		*3560*	1,500
	2760	30,000		3120	11,000			
	3480	1,500				(VI)	*2600*	30,000
	3650	1,500	(V)	2580	52,000		2700	34,000
				2810	12,000		2800	30,800
(II)	2510	30,500		2910	10,000		*3010*	13,000
	2580	33,000		3010	10,000		*3130*	10,000
	2670	30,500						
	3460	1,000	(VIII)	2580	38,000	(VII)	2700	36,000
	3640	1,000		2910	8,000		*2770*	32,000
				3020	11,500		*3040*	10,000
				3140	11,500			

(Italicised wave-lengths refer to inflections.)

It can be seen that the spectra fall into two well-defined groups. The first, comprising the aldehydo-acid (I), the ϕ-ester (II), the bishydroxymethyl compound (IV), the cyclic ether (V), and 4 : 5-dimethylphenanthrene itself (VIII), consists of absorption curves which are definitely " phenanthrenoid " in character, although some of the fine structure exhibited by phenanthrene itself has been smoothed out. This may be taken to indicate that in these compounds the steric hindrance associated with 4 : 5-substitution does not affect the uniplanarity of the phenanthrene nucleus. The second group, containing the methyl ester (III), the di*iso*thiuronium dibromide (VII), and the bisbromomethyl compound (VI), is characterised by a single region of maximal absorption with practically no fine structure. It would seem that in these three compounds with very bulky substituents at positions 4 and 5, there is considerable distortion of the phenanthrene nucleus with consequent inhibition of resonance.

Experimental.

4-Formylphenanthrene-5-carboxylic Acid (I).—A modification of the method of Vollmann *et al.* (*loc. cit.*) was adopted. Pyrene (10 g.) was dissolved in carbon tetrachloride (250 c.c.) and a stream of ozonised oxygen (5% O_3) was passed through the solution for 16 hours. As pyrene ozonide is insoluble in carbon tetrachloride, it is precipitated from the solution and is thus protected from further ozonisation. The carbon tetrachloride was then removed in steam, and the residue worked up as described by the German authors. From the reaction were obtained unchanged pyrene (5·8 g.) and the aldehydo-acid (3·7 g.; conversion 42%; yield 71%). The acid was recovered unchanged after treatment with alcoholic 2 : 4-dinitrophenylhydrazine sulphate and semicarbazide acetate.

4-Methyl Ester (II).—A suspension of the aldehydo-acid (1 g.) in methanol (40 c.c.) was saturated with hydrogen chloride and heated under reflux for 2 hours. The solvent was removed, and the residue treated with sodium carbonate solution. The insoluble material was crystallised from methanol, giving the *4-ester* (II) as needles, m. p. 176—177° (Found: C, 77·0; H, 4·6. $C_{17}H_{16}O_3$ requires C, 77·2; H, 4·6%). Like the parent acid, this ester exhibited no carbonyl reactivity.

Methyl Ester (III).—The finely-powdered aldehydo-acid (3·6 g.) was suspended in acetone (50 c.c.) and treated with an excess of ethereal diazomethane; the solution was kept at room temperature for 16 hours, all the solid then having dissolved. Removal of the solvent and crystallisation from methanol gave the *methyl ester* (2·9 g.) as needles, m. p. 113—114° (Found: C, 77·1; H, 4·8. $C_{17}H_{16}O_3$ requires C, 77·2; H, 4·6%). The action of methanolic 2 : 4-dinitrophenylhydrazine sulphate yielded the corresponding 2 : 4-*dinitrophenylhydrazone* as orange prisms, m. p. 250°, from methanol (Found: N, 12·65. $C_{23}H_{20}O_6N_4$ requires N, 12·6%).

No recognisable product was obtained from the attempted reduction of the ester by the Clemmensen and the Huang-Minlon procedure.

4 : 5-*Bishydroxymethylphenanthrene* (IV).—A mixture of powdered lithium aluminium hydride (8 g.), the methyl ester (III) (2·5 g.), and dry ether (200 c.c.) was heated under reflux for 30 minutes. The cooled reaction mixture was cautiously decomposed with ice and dilute sulphuric acid. Evaporation of the dried (Na_2SO_4) ethereal layer and crystallisation from benzene furnished the diol (2·25 g.) as needles, m. p. 152—159°. Recrystallisation from the same solvent effected little improvement in the wide melting range of the product (cf. Newman and Whitehouse, *loc. cit.*); possibly the azeotropic dehydrating effect of boiling benzene caused some conversion into the cyclic ether (V). A sharply melting specimen, m. p. 171—172°, was obtained by crystallisation from alcohol and heating the crystalline alcoholate thus obtained (Found: C, 80·6; H, 5·9. Calc. for $C_{18}H_{14}O_2$: C, 80·7; H, 5·9%). The *diacetate*, prepared by heating the diol with acetic anhydride and potassium acetate, crystallised from light petroleum (b. p. 100—120°) in prisms, m. p. 105° (Found: C, 74·6; H, 5·75. $C_{22}H_{18}O_4$ requires C, 74·55; H, 5·6%).

Cyclic Ether (V).—The above diol (1 g.) was dissolved in benzene (10 c.c.), a small quantity of anhydrous calcium chloride added, and the solution saturated with dry hydrogen chloride. Filtration, evaporation of the benzene, and crystallisation of the residue from light petroleum (b. p. 60—80°) gave an almost quantitative yield of the cyclic ether (V) as plates, m. p. 77—78° (Found: C, 87·3; H, 5·4. Calc. for $C_{18}H_{12}O$: C, 87·1; H, 5·8%). The 2 : 4 : 7-trinitrofluorenone *complex* (Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727) crystallised in orange prisms, m. p. 190—191°, from alcohol (Found: N, 7·7. $C_{32}H_{17}O_7N_3$ requires N, 7·9%).

4 : 5-*Bisbromomethylphenanthrene* (VI).—4 : 5-Bishydroxymethylphenanthrene (280 mg.), benzene (20 c.c.), and pyridine (10 mg.) were treated with phosphorus tribromide (600 mg.), and the mixture was warmed to 50° for 2 hours. The benzene solution was then washed with water and sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue of 4 : 5-*bisbromomethylphenanthrene* (370 mg., 85%) crystallised from benzene in prisms, m. p. 194° (decomp.) (Found: C, 52·6; H, 3·45; Br, 43·9. $C_{16}H_{12}Br_2$ requires C, 52·8; H, 3·3; Br, 43·8%).

Attempted reduction of (VI). (*a*) The bisbromomethyl compound (50 mg.), dissolved in acetone (10 c.c.), was shaken in an atmosphere of hydrogen with palladium–strontium carbonate catalyst (50 mg.; 2%). Removal of catalyst and solvent yielded a low-melting solid which was purified by sublimation at 10^{-4} mm. to give prisms, m. p. 75—76° undepressed on admixture with the cyclic ether (V). (*b*) 4 : 5-Bisbromomethylphenanthrene (500 mg.) was dissolved in benzene (20 c.c.) and slowly added to a boiling solution of lithium aluminium hydride (2 g.) in ether (250 c.c.) (cf. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3738). The solution was heated under reflux for 16 hours and carefully decomposed with ice and dilute sulphuric acid. Evaporation of the dried (Na_2SO_4) ethereal layer furnished a solid which sublimed readily at 70°/10^{-4} mm. giving prisms, m. p. 75—76° undepressed on admixture with the cyclic ether (V).

Diisothiuronium Dibromide (VII).—A solution of 4 : 5-bisbromomethylphenanthrene (100 mg.) and thiourea (64 mg.) in dry acetone (10 c.c.) was heated under reflux for 30 minutes. The precipitated white solid (136 mg., 96%) was filtered off and washed with a little acetone; it consisted of the *dibromide* (VII) in practically pure condition, m. p. 200—201°. Crystallisation from alcohol–acetone gave rosettes of needles, m. p. 200—201° (Found: C, 41·9; H, 4·0. $C_{18}H_{20}N_4Br_2S_2$ requires C, 42·0; H, 3·9%).

4 : 5-*Dimethylphenanthrene* (VIII).—A solution of the *diisothiuronium* dibromide (340 mg.) in alcohol (15 c.c.) was heated under reflux with Raney nickel (*ca.* 500 mg.) for 1 hour. Removal of catalyst and solvent gave a low-melting solid which was dissolved in light petroleum (b. p. 40—60°) and chromatographed over alumina. The movement of the sharp band formed was easily followed by means of its intense blue fluorescence in ultra-violet light. Development of the chromatogram with light petroleum washed the band through the column; evaporation of the solvent and crystallisation of the solid thus obtained from methanol gave 4 : 5-dimethylphenanthrene (150 mg., 76%) as prisms, m. p. 75—76° (Found: C, 93·4; H, 6·8. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). The 2 : 4 : 7-trinitrofluorenone complex crystallised from alcohol in scarlet needles, m. p. 120—121° (Found: N, 7·9. Calc. for $C_{30}H_{19}O_7N_3$: N, 8·1%). Fission of this complex by chromatography in benzene over alumina gave the parent hydrocarbon with m. p. identical with the sample obtained as above. The picrate, m. p. 109—110°, formed orange prisms from alcohol (Found: N, 9·75. Calc. for $C_{28}H_{17}O_7N_3$: N, 9·7%).

The above work was carried out during the tenure of an I.C.I. Fellowship (G. M. B.) and Maintenance Allowances of the Department of Scientific and Industrial Research (J. E. C., A. I. S.), for which we express our thanks.

UNIVERSITY OF GLASGOW. [*Received, June 12th*, 1950.]

478. *Colour and Constitution. Part I. Basic Dyes.*

By M. J. S. Dewar.

The calculation of light absorption by the molecular-orbital method is discussed, and reasons are given for believing that basic dyes should provide a favourable case for its application. This conjecture has been confirmed by agreement between the calculated and experimental absorption frequencies for a number of basic dyes. A general molecular-orbital theory of such dyes is proposed which leads to a comprehensive set of rules for the effect of structural changes on light absorption.

The relation between colour and constitution has been for decades an outstanding problem in organic chemistry, solution of which became feasible only with the development of the quantum theory. Exact treatment of complex molecules by the new methods is of course out of the question, but qualitative reasoning based on very approximate solutions of the relevant wave equations has provided some understanding of the basic processes involved in light absorption (cf. Forster, *Z. physikal. Chem.*, 1940, **48**, *B*, 12; Herzfeld and Sklar, *Rev. Mod. Physics*, 1942, **14**, 294; Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273; Lewis, *J. Amer. Chem. Soc.*, 1945, **67**, 770; Dewar, "The Electronic Theory of Organic Chemistry," Oxford, 1949). The purpose of the present paper is to put this qualitative treatment on a firmer basis.

Three approximate methods have been used to calculate the light absorption of conjugated organic compounds; the simple MO (molecular-orbital method), the VB (valence-bond method), and the ASMO (anti-symmetricalised molecular-orbital method). Of these the ASMO is the most rigorous and the most satisfactory, since explicit allowance is made for electron spin, and no empirical parameters are involved. The method was devised by Goeppert-Mayer and Sklar (*J. Chem. Physics*, 1938, **6**, 645) and was used by them to interpret the complete electronic spectrum of benzene; it has since been extended to diphenyl (London, *ibid.*, 1945, **13**, 396) and simple Wurster salts (Goeppert-Mayer and McCallum, *Rev. Mod. Physics*, 1942, **14**, 248), and further improved by Craig *et al.* (cf. *Proc. Roy. Soc.*, 1950, **200**, *A*, 474). For the present purpose the method is unsuitable, however, since it would involve prohibitively tedious calculations and would not yield the kind of qualitative generalisations sought. The VB method is unsuitable for calculating light absorption, since it is difficult to include ionic forms, and otherwise the calculated transitions have zero transition moments. No reliable conclusions could be drawn from a model so divorced from reality. Therefore the simple MO method has been used here, for lack of any practicable and better alternative.*

The simple MO method suffers from a number of major theoretical shortcomings (cf. Coulson and Dewar, Faraday Soc. Discussions, 1947, **2**, 54) but nevertheless seems quite satisfactory for calculating ground-state energies and electron distributions in hydrocarbons. Apparently the errors are reasonably constant and can be compensated by adjusting the empirical parameter in terms of which the energies are expressed. In molecules containing hetero-atoms, the method is less satisfactory, since the assumption of a self-consistent field breaks down (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193) but here too the results are reasonable if the additional parameters involved are given suitable values. In the calculation of light absorptions, however, the method often fails very badly. Two effects are probably largely responsible. First, the method neglects electron spin. Therefore it does not distinguish between a corresponding pair of singlet and triplet excited states but gives some kind of average of the two; the calculated excitation energies cannot be brought into correspondence with experiment by adjusting the empirical "resonance integral" since the singlet–triplet separation is neither constant nor in constant ratio to the mean excitation energy. Secondly, the failure of self-consistency will be more serious in excited states where the charge displacements tend to be large.

Now there are reasons for believing that both these effects may be smaller in the case of basic dyes. First, the singlet–triplet separations in such dyes seems to be unusually small (approximetly 6 kcals.; cf. Kasha, *Chem. Reviews*, 1947, **41**, 401). Secondly, the dyes contain more π-electrons than atoms; the accumulation of π-electrons on the terminal hetero-atoms (owing to their relatively high electron affinity) will be compensated by the extra electrons, and the central carbon chain should to a first approximation resemble that in a hydrocarbon. Naturally, these conjectures require confirmation, and so the light absorption of a representative range of basic dyes has been calculated by using one set of theoretically acceptable parameters.

* Kuhn's uniform potential model (cf. *Helv. Chim. Acta*, 1949, **32**, 2247) is even cruder than the simple MO model.

The results are compared with experiment in the Table. It will be seen that the agreement is surprisingly good, particularly since (i) no attempt has been made to choose the best values for

Compound.	$\lambda_{max.}$ (calc.).*	$\lambda_{max.}$ (obs.).*
$Me_2\overset{+}{N}{:}CH\cdot[CH{:}CH]_n\cdot NMe_2$; $n = 1$	3160	3090
$n = 2$	4390 2310	4090 2530
$n = 3$	5120 2900 1950	5110 3050 2660
Michler's hydrol blue	5850 (*x*) 4020 (*y*) 3440 (*x*)	6100 (*x*) 3600 (*y*) 3000 (*x*)
Malachite-green	6080 (*x*)	6160 (*x*)
Bindschedler's green	7740	7400
Crystal-violet	5590 (*x*) 3680 (*y*) 3250 (*y*) 2590 (*x*)	5910 5450 } (*x*) 3050 (*y*) 2500 (*x*)
Acridine-orange	4320	4910
2 : 7-Diaminophenazinium salts	5520	5130
Sodio-derivative of acetylacetone	2660	2900
Sodium derivative of dihydroresorcinol	2660	2800
$NaO\cdot[CH{:}CH]_2\cdot CH{:}N\cdot[CH{:}CH]_2\cdot CHO$	5680	5500

* Wave-lengths in A., to nearest 10A.

the various empirical parameters, (ii) the change in electron affinity of carbon adjacent to hetero-atoms has for simplicity been neglected, and (iii) the electron affinities of the hetero-atoms can be significantly altered by alkylation. Even the higher excited levels are correctly predicted in many cases; a few examples are given in the Table. The direction of the absorbed electric vector is also correctly predicted in cases when it is known experimentally. In *x*-bands the vector lies along the major axis, in *y*-bands along the minor axis, of the conjugated system [the observed values quoted in the Table are those given by Lewis and Bigeleisen (*J. Amer. Chem. Soc.*, 1943, 65, 2102, 2107), Simpson (*J. Chem. Physics*, 1948, 16, 1124), Schwarzenbach, Lutz, and Felder (*Helv. Chim. Acta*, 1944, 27, 576), and International Critical Tables].

Method.—**The calculations followed the standard procedure and require little comment. Overlap was neglected since preliminary calculations showed that its inclusion made little difference. The following values were ascribed to the various Coulomb terms (q relative to carbon) and resonance integrals (γ).**

q_N (in NR_2) $= \gamma_{CC}$ $\qquad$ $\gamma_{CN} = \gamma_{CC}$
q_N (in $RN{:}C$) $= 0{\cdot}5\ \gamma_{CC}$ $\qquad$ $\gamma_{CO} = \gamma_{CC}\cdot\sqrt{2}$
q_O (terminal) $= \gamma_{CC}$
$\gamma_{CC} = 73{\cdot}2$ kcals.

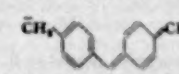
The calculations are confined to dyes where all the central atoms are carbon or nitrogen, since there is not sufficient evidence to determine the resonance integrals and Coulomb terms of oxygen and sulphur in dyes such as Pyronine G or methylene-blue.

The Coulomb terms (q) require some comment since they are less than the values assumed by other authors. Higher q's lead to excessive calculated dipole moments for simple >C=N and >C=O bonds. The higher values have been assumed in order to get correct calculated moments for more complex molecules; this situation probably arises from the inadequate allowance that has been made for the change in electron affinity of carbon atoms adjacent to hetero-atoms. Investigations by Branch and Calvin ("The Theory of Organic Chemistry," New York, 1946) and McGowan (*Nature*, 1947, 159, 644; *Chem. and Ind.*, 1948, 632) suggest that if the Coulomb term of a hetero-atom attached to a carbon chain is q, the carbon atoms along the chain should be ascribed Coulomb terms εq, $\varepsilon^2 q$, etc., where $\varepsilon \sim 0{\cdot}4$—$0{\cdot}5$. Most authors have assumed that $\varepsilon \leqslant 0{\cdot}1$ in carrying out MO calculations. The use of too small an ε will affect energy calculations little, but it will destroy the value of calculations of dipole moments. Calculations

of rates of benzene substitution, with a more reasonable value of s ($\frac{1}{2}$), suggest that $q < 2$ for all the usual hetero-atoms (Dewar, *J.*, 1948, 463).

General Theory of Basic Dyes.—The next step, the main purpose of this paper, will be the development of a general qualitative theory of colour in basic dyes.

A basic dye can be formally derived from a mesomeric carbanion by replacing carbon atoms by hetero-atoms and by introducing substituents. It will be assumed that the effects of such changes on the light absorption of the ion are additive (this assumption is equivalent to a first-order perturbation treatment, and it can also be justified empirically; cf. Lewis and Calvin, *loc. cit.*). For instance, Acridine-orange (I) would be formally derived from the carbanion (II) by substitution with NMe and replacement of the terminal CH_2 groups by NMe_2.

(I.) (II.) 

The following treatment makes use of some results of Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39), and of a modification of the usual MO methods (Dewar, *Proc. Camb. Phil. Soc.*, 1949, **45**, 638). In this LCMO (linear combination of molecular orbitals) modification, the secular equation of a conjugated molecule RS is set up by using the MO's calculated for RH and SH as trial eigenfunctions. The final secular equation must be identical with that given by the usual LCAO method, but the LCMO determinant can be expanded explicitly to give this equation in a particularly convenient form.

Several theorems will now be established for the effect of structural changes on the light absorption of carbanions. It will be assumed that the molecules are alternant (Coulson and Rushbrooke, *loc. cit.*), and that the terminal atoms, *e.g.*, CH_2 in (II), belong to the "starred" set. Only the frequency of the first absorption band (FFAB) will be discussed, since this determines the general colour of a dye.

(a) *The* FFAB *of the hydrocarbon* R–S *is not greater than the* FFAB *of* RH *or* SH *provided that* RH *and* SH *are not both odd.* Denote the π-MO's of RH by Ψ_r, of SH by Φ_s, where

$$\Psi_r = \sum_m a_{rm}\phi_m, \quad \Phi_s = \sum_n b_{sn}\phi_n$$

and where the total numbers of ϕ's and of ϕ's are even. Let the energies of Ψ_r, Φ_s be E_r, F_s respectively, in units of γ_{CC}, the CC resonance integral. Then if, in RS, R and S are linked through atom j in R and atom k in S, the secular equation of RS may be shown to be (Dewar, *loc. cit.*):

$$\prod_r (W - E_r) \prod_s (W - F_s) \left\{ 1 - \sum_r \frac{a_{rj}^2}{W - E_r} \sum_s \frac{b_{sk}^2}{W - F_s} \right\} = 0 \quad . \quad . \quad . \quad (1)$$

It may be assumed that no root of (1) is equal to an E_r or F_s, since equality can occur only if RH or SH has degenerate levels, or if one of the a_{rj} or b_{sk} vanishes—in either case the identical roots can be explicitly factored out of (1), leaving an equation of the same form.

Now Coulson and Rushbrooke (*loc. cit.*) have shown that the roots of the secular equation for a hydrocarbon occur in pairs with energies equal in magnitude but opposite in sign, and that the coefficients of the atomic orbitals in the corresponding MO's again differ at most in sign. Equation (1) may therefore be written

$$1 - \sum_r \left\{ \frac{a_{rj}^2}{W - E_r} + \frac{a_{rj}^2}{W + E_r} \right\} \sum_s \left\{ \frac{b_{sk}^2}{W - F_s} + \frac{b_{sk}^2}{W + F_s} \right\} = 0,$$

or

$$1 - 4W^2 \sum_r \frac{a_{rj}^2}{W^2 - E_r^2} \sum_s \frac{b_{sk}^2}{W^2 - F_s^2} = f(W) = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the smallest E_r^2 or F_s^2 is ϵ^2, then as W^2 increases from 0 to ϵ^2, $f(W)$ decreases from $+1$ to $-\infty$. Therefore equation (2) has roots $\pm g$ where $g^2 < \epsilon^2$. Now the lowest excitation energy of RH or SH is $2|\epsilon|$, if overlap is neglected, and the lowest excitation energy of RS is $2|g|$. Since $|g| < |\epsilon|$, the FFAB of RS must be less than that of RH or SH. This conclusion is not altered by inclusion of overlap; the excitation energies become:

$$\frac{2|g|}{1 - S_g^2} < \frac{2|\epsilon|}{1 - S^2\epsilon^2},$$

and these obey the indicated inequality (since $S^2\epsilon^2 < 1$).

The only exception occurs when the lowest level of (RH + SH) factors out of the secular equation for RS; here RS has the same FFAB as the lower FFAB of RH or SH.

This completes the proof of the theorem for normal hydrocarbons; the proof for the case where RH or SH has an odd number of conjugated atoms (*i.e.*, is an ion or radical) is so nearly identical that it need not be given. The theorem does not hold if both RH and SH are odd.

(b) ***Replacement of an unstarred carbon atom in the carbanion*** R^- ***by a hetero-atom lowers the*** FFAB. Let the jth carbon atom in R^- be replaced to give R_H^-. Let the Coulomb term of the hetero-atom be q relative to carbon. Then, to a first approximation, the change δE_r in the energy level E_r will be given (cf. Coulson and Longuet-Higgins, *loc. cit.*) by:

$$\delta E_r \simeq -q\partial E_r/\partial q_j = -q \cdot a_{rj}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now for the highest occupied orbital in R^-, $a_{rj} = 0$ (Coulson and Rushbrooke, *loc. cit.*). This orbital remains unchanged in R_H^-, to a first approximation. The energy of the first excited level in R_H^- will, from equation (3), be less than that in R^-, since $q > 0$. Therefore the FFAB of R_H^- is less than that of R^-.

(c) ***Replacement of a starred atom in*** R^- ***by a hetero-atom will usually raise the*** FFAB. If the highest occupied and the lowest unoccupied MO in R^- are the rth and sth respectively, it follows from equation (3) that the excitation energies for $R^-(E)$ and $R_H^-(E_H)$ are related by the expression

$$E_H - E \simeq q(a_{rj}^2 - a_{sj}^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since the rth MO is confined to only half of the conjugated atoms in R^-, while the sth MO covers the whole molecule, it is likely that $|a_{rj}| > |a_{sj}|$. Therefore as a rule, R_H^- will have a higher FFAB than R^-.

(d) ***The effects in*** (b) ***and*** (c) ***are roughly proportional to*** q. This follows at once from equations (3) and (4).

(e) ***A*** $-$E (***anionoid electromeric***) ***substituent in*** R^- ***at an unstarred carbon raises the*** FFAB. Consider the case of a monatomic substituent X, with Coulomb term q, attached to atom j in R^-. The secular equation for $(RX)^-$ is (Dewar, *loc. cit.*):

$$W + q - \sum_r \frac{a_{rj}^2}{W - E_r} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Applying a first-order perturbation treatment for the root corresponding to E_r, we have:

$$(E_r)_H \simeq E_r + [a_{rj}^2/(E_r + q)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This shows that addition of the substituent "repels" the roots from the level $-q$. [(RX) will have root approximately equal to $-q$ in addition to the roots approximately equal to E_r.] At an unstarred position, however, if $q > 0$ (as is always the case), $a_{rj} = 0$ for the highest occupied level; this level remains unchanged in $(RX)^-$ to a first approximation. But the lowest unoccupied level is raised [cf. equation (6)]. Therefore the FFAB of (RX^-) is greater than that of R^-. It is easily shown that the same is true if X is attached to two unstarred atoms in R, forming a ring, and that inclusion of overlap does not affect the results.

(f) ***A*** $-$E ***substituent at a starred atom will tend to lower the*** FFAB. This result follows from equation (6) in the same way that (*c*) follows from equation (3).

(g) ***The effects in*** (e) ***and*** (f) ***decrease with increasing*** q. This follows at once from equation (6).

(h) ***A*** $+$E (***cationoid electromeric***) ***substituent should tend to lower the*** FFAB. The introduction of such a substituent $\cdot X{:}Y$ can be supposed to take place in stages. First introduce $\cdot CH{:}CH_2$, then replace CH by X, then CH_2 by Y. The first step will lower the FFAB [(a) above]. Of the other two steps, one will raise, and one will lower, the FFAB, but the latter, a first-order effect [(b) above] should in general be greater than the former, a second-order effect [(c) above]. Therefore the net effect of the $+E$ substitutent should be to lower the FFAB. The relative effects of such substituents in starred and unstarred positions can be predicted, using the rules already given. Thus $\cdot COR$ should have a greater bathochromic effect in an unstarred position, since the oxygen is then unstarred. There do not seem to be any suitable data available to check such predictions.

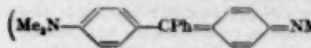
General Conclusions.—The results of the foregoing analysis may be summed up in the following generalisations. It is assumed that the dye is formally derived from a carbanion by

substitution or replacement, and that the terminal atoms in the carbanion are starred. Then the FFAB will in general be lowered by (1) extension of the conjugated system, (2) replacement of unstarred carbon by a hetero-atom, (3) substitution of starred carbon by a $-E$ group, or (4) $+E$ substituents. In (2) the effect should be greater, in (3) less, the greater the electron affinity (q) of the hetero-element or $-E$ group. (It is of course assumed that replacement does not alter the total number of π-electrons; thus only terminal carbon can be replaced by hetero-elements other than nitrogen.)

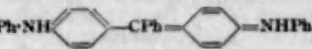
The FFAB will be raised by (5) replacement of starred carbon by a hetero-atom or (6) substitution of unstarred carbon by a $-E$ group. The effect in (5) should be greater, in (6) less, the greater the electron affinity of the hetero-element or $-E$ group.

Comparison with Experiment.—All these conclusions seem to agree with experiment, and many of them are already known empirically. One or two examples will suffice in each case.

(1) This well-known effect is seen most clearly in the cyanine dyes, where the FFAB falls as n increases in the sereies $[R\cdot[CH{:}CH]_n\cdot S]^+$. An interesting further example is the decrease in



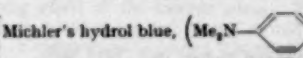
(III.) $\lambda_{max.} = 6160$.

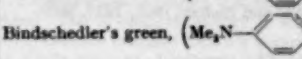


(IV.) $\lambda_{max.} = 6370$.

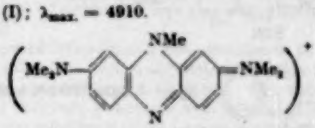
FFAB brought about by terminal arylation, *e.g.*, in the pair Malachite-green (III) and Viridine-green (IV). Here the effect of additional conjugation outweighs the effect of increasing the electron affinity of the nitrogen atoms.

(2)

Michler's hydrol blue,  ; $\lambda_{max.} = 6100$.

Bindschedler's green,  ; $\lambda_{max.} = 7400$.

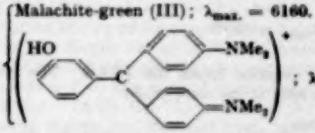
Acridine-orange (I); $\lambda_{max.} = 4910$.

Methylene-blue,  ; $\lambda_{max.} = 5645$.

In each case replacement of unstarred C by N lowers the FFAB.

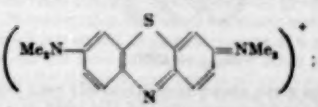
(3)

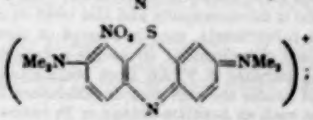
Malachite-green (III); $\lambda_{max.} = 6160$.

 ; $\lambda_{max.} = 6174$.

Addition of a $-E$ substituent (OH) at a starred position lowers the FFAB.

(4)

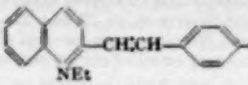
Methylene-blue  ; $\lambda_{max.} = 6084$.

Methylene-green  ; $\lambda_{max.} = 6580$.

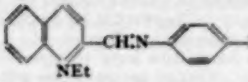
The $+E$ substituent (NO_2) lowers the FFAB.

(5) Since the terminal groups in a dye are starred, this rule implies that the FFAB should be raised by increasing the electron affinity (decreasing the basicity) of the terminal groups. This

effect is qualitatively very well known (see Dewar, *op. cit.*, for numerous examples). The effect of replacing central starred atoms is seen in the following comparisons :

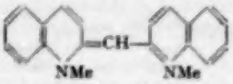


: $\lambda_{max.} = 5300$.

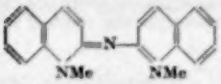


: $\lambda_{max.} = 5900$.

(the mean shift for ten such pairs is 400 A.; Bloch and Hamer, *Phot. J.*, 1930, **54**, 374).

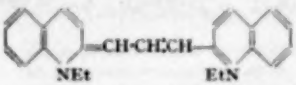


: $\lambda_{max.} = 5230$.

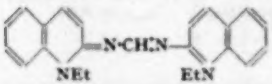


: $\lambda_{max.} = 4240$ (Hamer, *J.*, 1924, **125**, 1348).

(The mean shift for three such pairs is 900 A.; Fisher and Hamer, *ibid.*, 1927, 907).



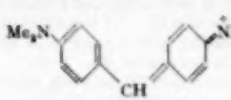
: $\lambda_{max.} = 6050$.



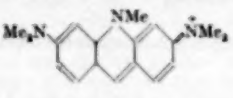
: $\lambda_{max.} = 3430$ (Fisher and Hamer, *loc. cit.*).

(6) { Malachite-green (III) ; $\lambda_{max.} = 6160$.
{ Crystal-violet, $(Me_2N{-}C_6H_4{-})_3C^+$, $\lambda_{max.} = 5905$.

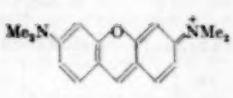
Addition of a $-E$ group (NMe_2) at an unstarred position raises the FFAB. The effect of increasing the electron affinity of the substituent is seen in the comparison :



$\lambda_{max.} = 6100$.



$\lambda_{max.} = 4910$.



$\lambda_{max.} = 5475$.

Conclusions.—Some of the rules given above have previously been put forward on qualitative grounds but the present discussion is more complete and also rests on a much firmer theoretical basis. The alternating effect of substituents, etc., in starred or unstarred positions has not been noticed previously as a general phenomenon; its nature is brought out very clearly in the present treatment. The striking increase in FFAB from Malachite-green to Crystal-violet is also well interpreted, and also of course the still greater differences between Michler's hydrol blue and analogous tricyclic dyes such as Acridine-orange or Pyronine G.

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479. *The Molecular-orbital Treatment of Organic Compounds containing Oxygen.*

By J. G. M. Bremner and (Mrs.) W. C. G. Bremner.

It is shown that the method of molecular orbitals gives reasonable values for the resonance energy of a variety of conjugated systems involving oxygen, provided that an adjustment to the Coulombic term of the oxygen atom is made. An interesting result is that this adjustment has little effect on the magnitude of the additional resonance energy calculated for vinylfuran and the furfuryl radical. It is further pointed out that, in the related hydrocarbon R·CH=CH$_2$ and group R·CH$_2$·, the additional resonance energy, calculated by the molecular-orbital method, is not only little dependent on the resonance energy of the group R, whether it be aliphatic or cyclic in character, but is also similar to that of the furan compounds.

Some cyclic nitrogen compounds are also considered.

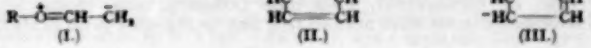
Molecular-orbital calculations overestimate the resonance energy of oxygen-containing compounds if no allowance is made for the greater electron affinity of the oxygen atom compared with carbon (cf. Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2091). When this effect is ignored, the localisation of electrons on the oxygen atom is neglected and hence the derived binding energy is too large. Thus simple molecular-orbital treatment gives 2·48β for the resonance energy of furan and 1·46β for divinyl ether, compared with the empirical values of about 1β and 0·2β, respectively (where β, the C–C resonance integral, is considered to be 18 kcals.). It is the object of this paper to examine the molecular-orbital treatment of oxygen-containing compounds with the aim of establishing the simplest modification necessary to allow for the disturbing effect of the oxygen atom. The compounds treated include furan and pyran derivatives, vinyl ethers, and phenol, as well as the furfuryl radical.

The calculations were carried through in the usual manner and therefore require no detailed description. The π electron energy is expressed only in terms of the β component. The empirical resonance energies used for comparison were derived from heats of hydrogenation or heats of combustion (cf. Wheland, "The Theory of Resonance," John Wiley & Sons, 1944). For furan, a group method of estimation was also used (Bremner and Thomas, *Trans. Faraday Soc.*, 1948, **44**, 230, 338)

Comparison of Suggested Methods.—Three modifications to the simple molecular-orbital treatment were considered. The first modification attempts to allow for the localisation effect by arbitrarily reducing the number of electrons. The second is based on a suggestion by Wheland (*op. cit.*, p. 52) that only structures with adjacent formal charges are significant. The third allows for the electro-negativity of the oxygen atom by adjustment of the parameters used in the molecular-orbital calculations (cf. Wheland and Pauling, *loc. cit.*; Evans, Gergely, and de Heer, *Trans. Faraday Soc.*, 1949, **45**, 312).

(i) *Reduction in the number of π electrons.* Initially, it seemed feasible to allow arbitrarily for the electron affinity of the oxygen atom by working with less than the normal number of electrons used in the simple molecular-orbital treatment. By this means the binding energy of the molecule and consequently its resonance energy would be reduced, as is required. Furan seemed to respond well to this method of approach if two of the six π electrons were disregarded in the calculation. As the two lowest roots of the relevant secular equation are -2β and $-0{\cdot}62\beta$, the π-electron energy now becomes $4{\cdot}24\beta$, and consequently the resonance energy—referred to two C–C double bonds—is $1{\cdot}24\beta$. This figure is in good agreement with the empirical values $0{\cdot}95\beta$, $1{\cdot}13\beta$, and $1{\cdot}28\beta$ derived from heats of hydrogenation, group calculations, and heats of combustion, respectively. However, this method of approach could be of value only if the correction for the localisation of electrons on the oxygen atom was of a general nature. Further consideration showed that this did not hold. Thus for vinyl ether the second orbital, and for phenol the fourth orbital, is neither bonding nor anti-bonding (*i.e.*, $W = 0$) and, in consequence, a reduction by two in the number of electrons now leaves unchanged the derived resonance energy in both instances.

(ii) *Consideration of only adjacent formal charges.* In discussing the small resonance energy of the vinyl ethers, relative to furan, Wheland (*op. cit.*) pointed out that the formal charges are separated in the ionic structures (I) ascribed to the former, but can be on adjacent atoms for the

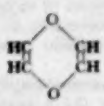


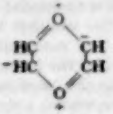
(I.) (II.) (III.)

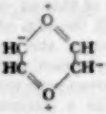
furan structure as in (II). He suggested, in consequence, that the main contribution to the stabilisation of the furan molecule is due to structures such as (II) and that those such as (III), in which the formal charges are separated, play only a small part. A relatively high electron density in the 2-position is, moreover, in accord with the orientation effects observed in substitution reactions. This view can be placed on a quantitative basis. Furan, for example, can be represented by the 3-orbital–4-electron systems shown in (IV) and (V). The resonance energy of the corresponding hydrocarbon analogue—the allyl anion—is 0·83β, in fair agreement

(IV.) (V.)

with the empirical values for furan. In the same manner, 2-vinylfuran would be represented by a 5-orbital–6-electron system for which an additional resonance energy, above that for the furan molecule, of 0·64β was derived. This is, however, about twice the empirical energy 0·3β, and is in poorer agreement than the simple molecular-orbital treatment which, somewhat surprisingly, gives the low value, 0·44β. Furthermore, the dioxadien molecule (VI) would presumably be accorded an unacceptably large resonance energy on Wheland's view, as two pairs of adjacent charges are present in the ionic structures (VII) and (VIII) (Summerbell and Umhoefer, *J. Amer. Chem. Soc.*, **1939**, **61**, 3020).


(VI.)


(VII.)


(VIII.)

In general it is felt that Wheland's suggestion, while often of value in a qualitative way, is unlikely to form a useful basis for quantitative treatment. Modified parameters could be introduced in the calculations to allow for the electron affinity of the oxygen atom, but such refinements hardly seem justified.

(iii) *Modifications to the parameters of the secular equation.* As mentioned above, an allowance for the disturbing effect of an oxygen atom can be made by modifying the parameters involved in the simple molecular-orbital treatment (Wheland and Pauling, *loc. cit.*). Such modifications can comprise an adjustment of the Coulomb terms of the oxygen and the adjacent carbon atoms and of the resonance integral for the C–O bonds relative to the C–C bonds. In particular, Wheland and Pauling have made adjustments to the first two parameters in their quantum-mechanical treatment of orientation in the furan nucleus. We now consider the effects of such adjustments on the derived resonance energy of a number of oxygen-containing compounds.

Results obtained by using Modified Parameters.—Furan was taken as the test material in order to assess the dependence of the resonance energy on the magnitude of the Coulombic term assigned to the oxygen atom. The results, given in Table I, show that a change from the normal value W to $(W + 2\beta)$ almost halves the derived resonance energy, while a further modification to $(W + 4\beta)$ produces a relatively small change. The use of the latter term, moreover, yields a resonance energy of 1·1β, close to the empirical value as Wheland and Pauling implied in their paper.

TABLE I.

Calculated values for the resonance energy of furan.

Coulombic terms for the oxygen atom.	Energy (β). Resonating molecule.	Non-resonating molecule.	Resonance energy (β).
W	6·48	4	2·48
$W + 2\beta$	9·37	8	1·37
$W + 4\beta$	13·1	12	1·1

As a consequence, the term $(W + 4\beta)$ was retained and an examination made of the effect of varying the Coulombic term for the carbon atoms in positions 2 and 5. The results obtained show the calculated resonance energy to be insensitive to variations in the range W to $(W + 0{\cdot}5\beta)$ (Fig. 1). Consequently, while these Coulombic terms require adjustment to account for substitution in the furan nucleus, they may be neglected so far as the derivation of

resonance energies is concerned. Naturally, such an adjustment becomes more significant in resonating systems smaller than furan—as, for example, vinyl ether (Table II)—but the decrease which accompanies its use will tend to be offset by the increase which would obtain if a larger resonance integral for the C–O bond were used. Such a modified resonance integral is formally required, as the difference between the strengths of the C=O and C–O bond is about twice that for the C=C and C–C bond. On the whole, therefore, it seemed reasonable to consider only an adjustment to the Coulombic term of the oxygen atom, particularly as this leaves the calculations relatively simple. To test this view, calculations were carried through for a number of oxygen-containing compounds of known resonance energies. The results are given in Table II which includes, for comparison, the values given by the unmodified molecular-orbital method. The latter are, as expected, uniformly too large, most noticeably so with divinyl ether which has the low empirical resonance energy of 0·2β.

TABLE II.

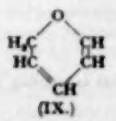
Resonance energies of vinylfuran, phenol, and the vinyl ethers.

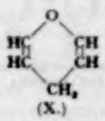
	Coulombic term for the oxygen atom.	Energy (β). Resonating molecule.	Non-resonating molecule.	Resonance energy (β). Calc.	Empirical.
Vinylfuran	W	8·92	8·48	0·44	—
	$W + 4\beta$	13·57	13·1	0·47	0·3 [b]
Ethyl vinyl ether	W	2·83	2	0·83	—
	$W + 4\beta$	10·20	10	0·20	—
	$W + 4\beta$	10·34	10·56	−0·22 [a]	—
	$W + 4\beta$	11·29	10·56	0·73 [b]	0·2
Phenol	W	8·72	8	0·72	—
	$W + 4\beta$	16·19	16	0·19	0·45 [c]
Divinyl ether	W	5·46	4	1·46	—
	$W + 4\beta$	12·48	12	0·48	0·2

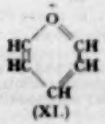
[a] "Strain" energy, calculated by using $(W + \frac{1}{2}\beta)$ on the carbon atoms adjacent to oxygen. [b] Calculated as above, but by use, in addition, of 2β for the C–O resonance integral. [c] Additional resonance energy.

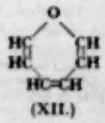
The modified values are generally much lower, as is required, and are in fair agreement with the empirical figures. The least satisfactory is divinyl ether where the calculated resonance energy is twice the small empirical value. A change in the Coulombic term, from W to $(W + \frac{1}{2}\beta)$, on the carbon atoms adjacent to oxygen would reduce the calculated resonance energy as required, but the use of such an adjustment would then result in poorer agreement for the other compounds. With ethyl vinyl ether, for example, a "strain" and not a resonance energy would be derived by its use (see Table II). In consequence it was decided to work only with the modified Coulombic term $(W + 4\beta)$ for the oxygen atom in the subsequent calculations.

Consideration of Various Heterocyclic Compounds.—Among the heterocyclic compounds to be considered are those containing oxygen, with structure (IX)–(XII). The unmodified molecular-


(IX.)


(X.)


(XI.)


(XII.)

orbital treatment ascribes a resonance energy of 1·46β to 2-pyran (IX), a value larger than the empirical value for furan. Such a value seems quite inconsistent with the failure of attempts to prepare the substance. A much lower and more satisfactory value, 0·68β, is given by the modified treatment. 4-Pyran (X) is accorded the same high stability as 2-pyran on the unmodified treatment, but an even lower resonance of 0·48β by the corrected method. The *cyclo*diene structure (VI), previously considered, may now be re-examined. It should have the same high stability as benzene, according to the unmodified method, but a figure of 0·75β, in much better agreement with its behaviour, is given by the corrected method (Beach, *J. Chem. Physics*, 1941, **9**, 541).

The disturbing effect produced by oxygen in lowering the resonance energy of a conjugated system will become less pronounced as the size of the system increases. As an interesting example, the pyrylium cation (XI) was treated by both methods. The calculated resonance energy decreased only from 2β to 1·74β. Naturally, apart from this high degree of internal

stability, a full treatment of such an ionic structure would involve consideration of its lattice and solvation energies.

A further example of the larger conjugated system is the seven-membered cyclic triene (XII). Its hydrocarbon analogue is the *cyclo*heptatrienyl anion whose resonance energy, by molecular-orbital calculations, is 2·1β (Hückel, The Physical Society, "Internat. Conf. on Physics," 1935, **2**, 9). The modified method of calculation applied to (XII) will reduce this value, but to an extent smaller than that previously noted for the corresponding pair, *cyclo*pentadienyl anion and furan, where the change is from 2·48β to 1·1β (Table I). In consequence, (XII) is likely to have a resonance energy about 1β. In agreement with this, calculation gives the value $(15{\cdot}28 - 14{\cdot}0)\beta = 1{\cdot}28\beta$, which is higher than that for furan. In addition to the *cyclo*heptatrienyl structure, a number of other structures may be used as a basis for estimating the resonance energy of (XII). Such comparative methods may be useful when the empirical or calculated value is unknown. The details of these methods are summarised in Table III, which also indicates where calculated or empirical values are used and whether the top molecular orbital is bonding or anti-bonding in type.

TABLE III.

Resonance energy of the cyclic triene (XII) *by comparative methods.*

Comparison no.	Replacement procedure.	Modification corresponding to (XII) Structure.†	Resonance * energy (β).	Related change. Structures.†	Resonance * energy change (β).	Deduced resonance energy of (XII) (β).
1	-O- by $\bar{C}H$	$\bar{C}H$ (*A*)	2·1 (m.o.)	$\bar{C}H$ (*B*) to O (*B*)	2·48 (m.o.) to 1·1 (e)	~1
2	-O- by -CH=CH-	(*Z*)	1·68 (m.o.)	O (*B*) to O (*B*)	2 (e) to 1·1 (e)	~1
3	-O- by $-CH_2-$	CH_2 (*B*)	0·3 (e)	CH_2 (*B*) to O (*B*)	0·16 (e) to 1·1 (e)	~2
4	—	$\bar{C}H$ (*A*)	2·1 (m.o.)	$\bar{O}$ (*B*) to O (*B*)	2·0 (e) to 1·74 (e)	~2

* (m.o.) indicates a calculated and (e) an empirical resonance energy.

† (*A*) represents a top molecular orbital which is anti-bonding, (*B*) one that is bonding, and (*Z*) one that is neither bonding nor anti-bonding.

When *cyclo*octatetraene is taken for comparison 2 (Table III), the resonance energy (1·68β) calculated for the planar molecule is used rather than the small empirical energy (0·3β) for the actual buckled molecule (Prosen, Johnson, and Rossini, *J. Amer. Chem. Soc.*, 1949, **69**, 2068).

It will be observed that the comparisons given in Table III place the resonance energy of (XII) in the range 1—2β. The reliability of the individual methods is not, however, the same. It will be less where the comparison of one structure having only bonding molecular orbitals is made with others which have non-bonding or anti-bonding molecular orbitals. This criticism applies to methods (1), (2), and (4). Method (3) is unsatisfactory because it involves a comparison of an open-chain resonating group with a cyclic group. Moreover, in (1) and (4) both charged and neutral molecules are involved in the comparison. In spite of these criticisms, it is evident that the comparative method gives a fair indication of the resonance energy in this instance.

In some instances, heterocyclic nitrogen compounds may also be considered on the present basis. As the electron affinity of nitrogen—though less than that of oxygen—is greater than

that of carbon, the replacement of a CH group by a nitrogen atom should reduce the resonance energy * (cf. Dewar, *Trans. Faraday Soc.*, 1946, **42**, 754). This particular replacement is, moreover, normally taken as leaving the resonance integral unchanged (Coulson and Longuet-Higgins, *Trans. Faraday Soc.*, 1947, **43**, 43; Coates and Sutton, *J.*, 1948, 1187). Thus it is customary to use only a modified Coulombic term ($W + 2\beta$), for the nitrogen atom, which indeed gives a suitable value for the resonance energy of pyrrole, at about 1·5β (cf. Table I). As an

FIG. 1.

The effect on the derived resonance energy of modifying the Coulomb term for carbon atoms 2- and 3- in furan.

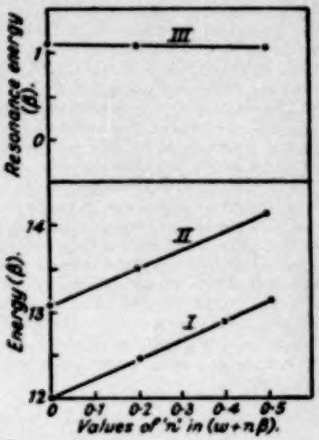


FIG. 2.

Comparison of additional resonance energy of vinyl derivatives and free methylene radicals with the resonance energy of the ring to which they are attached.

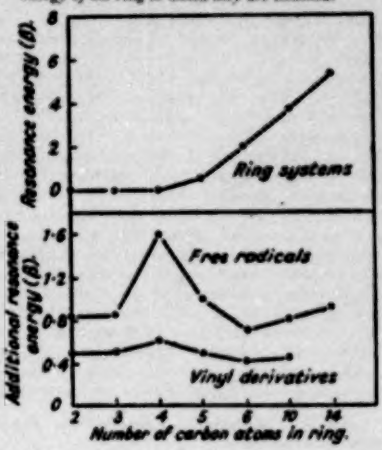
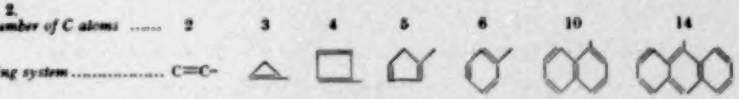


FIG. 1.
I, *Energy of lowest non-resonating structure.* II, *Ground-state energy.* III, *Resonance energy.*

FIG. 2.



example, the substitution of nitrogen for the relevant CH group in (IX) gives 1 : 4-oxazine which like the parent, 2-pyran, is also unknown. In view of its low resonance energy, we would not therefore expect 1 : 4-oxazine to be formed by the dehydrogenation of morpholine, its tetrahydro-derivative.

Finally, calculations were made for the furfuryl radical and radical ions (see Table IV). In particular, they show the resonance energies of the free radical and the cation to be little affected by the use of the modified Coulombic term on the oxygen atom. It is unfortunate that no experimental values are available for comparison.

Discussion.—While the resonance energy of furan is less than that calculated by the simple molecular-orbital method, the results given in Tables II and IV show the additional resonance energy of vinylfuran and of the furfuryl radical to be almost the same whether the simple or the modified molecular-orbital treatment is used. While such a result may be dependent on the basic assumptions of the methods used, it implies, if real, the additional resonance energy ascribed to an appendage to be almost independent of the resonance energy of the group to which the appendage is attached. Such a conclusion is, in fact, borne out by calculation in the hydrocarbon field. Thus the additional resonance energies, given by the molecular-orbital method, for both

* Empirical values for some 6-ring nitrogen compounds, *e.g.*, pyridine, are not apparently consistent with this statement. This may be due to the over-estimation of resonance energies in five-membered rings by the molecular orbital method (Syrkin and Diatkina, *Acta. Physicochim. U.R.S.S.*, 1946, **21**, 641).

TABLE IV.

The resonance energies of the furfuryl radical anion and cation.

Derivative.	Coulombic term for the oxygen atom.	Energy (β). Resonating molecule.	Non-resonating molecule.	Resonance energy (β).
Free radical	W	7·21	6·48	0·73
	$W + 4\beta$	13·97	13·10	0·87
Anion	W	6·96	6·48	0·48
	$W + 4\beta$	13·90	13·10	0·80
Cation	W	7·46	6·48	0·98
	$W + 4\beta$	14·04	13·10	0·94

the vinyl and the methylene group attached to ring systems varying from ethylene (a two-membered " ring ") through *cyclo*propene and *cyclo*butadiene to naphthalene and anthracene are shown in Fig. 2. But for a curious jump for the (unknown) *cyclo*butadiene derivatives, the additional resonance energy of the vinyl derivatives is around 0·4β (cf. Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, 195, 188), whereas the value for the substituted methyl derivatives is about twice as great (around 0·8β), and this, even when the resonance energy of the ring systems varies from 0β to 5β. The same conclusion can be drawn from molecular-orbital calculations for conjugated olefin structures, where the corresponding additional resonance energies tend to 0·54β and 1·27β, respectively, as the chain length increases (Hückel, *loc. cit.*). While these values seem qualitatively correct for vinyl compounds, in view of their ready polymerisation, they are somewhat larger than the empirical resonance energies, where comparison is possible. By contrast, the calculations give too low a value for the resonance energy of the free benzyl radical (cf. Szwarc, Faraday Soc. Discussion, 1947, **2**, 39). However, the approximate constancy of the resonance energies derived in these calculations seems to agree with experiment, as indicated by the results for the allyl, 2-methylallyl, benzyl, and picolyl free radicals (Szwarc *et al.*, *J. Chem. Physics*, 1948, **16**, 128, 981; 1949, **17**, 284, 292; Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339). As the calculated values for vinylfuran and the furfuryl radical are similar to those derived for the corresponding hydrocarbons, it appears, somewhat surprisingly, that little change in self-polarizability can result from the presence of the ring oxygen atom (Coulson and Longuet-Higgins, *loc. cit.*).

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3, LINDEN AVENUE, STOCKTON-ON-TEES, CO. DURHAM. [*Received, March 20th*, 1950.]

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480. *New Observations on the Elbs Persulphate Oxidation.*

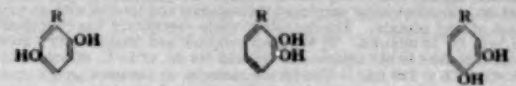
By J. FORREST and V. PETROW.

Elbs persulphate oxidation of phenols has yielded appreciable quantities of catechols (II) in addition to quinols (I). *m*-Substituted phenols have likewise been converted into derivatives of types (I) and (II), 4-substituted catechols (III) not being obtained.

THE formation of dihydric phenols by oxidation of monohydric phenols with potassium persulphate in alkaline solution, discovered by Elbs (*J. pr. Chem.*, 1893, [ii], **48**, 179), has formed the subject of numerous publications (see Baker and Brown, *J.*, 1948, 2303, for a brief review). The reaction involves the intermediate formation of a potassium hydroxyphenyl sulphate which is subsequently hydrolysed in acid solution to a quinol, a fact elegantly exploited by Baker and Brown (*loc. cit.*) for the preparation of quinol monomethyl ethers. Although the reaction mechanism proposed by the latter authors would lead one to expect the simultaneous formation of catechol and quinol derivatives from suitably constituted phenols, only quinols have hitherto been obtained; the formation of catechols, in somewhat lower yield, has been limited to cases in which the *para*-position was occupied.

We have recently had occasion to study the preparation of gentisic acid (I; R = CO_2H) by the Elbs persulphate oxidation of salicylic acid (cf. Mauthner, *J. pr. Chem.*, 1940, **156**, 150). Although the expected oxidation product was readily obtained in the crude state, purification presented difficulty owing to the presence of a persistent acidic impurity. However, fractional distillation of the derived methyl esters led to ready separation of methyl catechuate (II; R = CO_2Me) in *ca.* 15% of the total yield of dihydroxy-acid.

o-Nitro- and o-chloro-phenol and salicylaldehyde each similarly gave the catechol (II) and the quinol (I) derivatives (contrast Elbs, *loc. cit.*; Schering, G.P. 81,086; Baker and Brown, *loc.*



(I.) (II.) (III.)

cit.; and Neubauer and Flatow, *Z. physiol. Chem.*, 1907, **52**, 380. Further, *m*-substituted phenols [*m*-hydroxy-benzaldehyde (Hodgson and Beard, *J.*, 1927, 2339) and -benzoic acid] gave compounds of type (I) with smaller quantities of compounds of type (II); 4-substituted catechols (III) could not be isolated.

Potassium persulphate proved, in general, a more reliable oxidising agent than the corresponding ammonium salt (cf. Baker and Brown, *loc. cit.*), which gave variable total yields, but did not materially affect the proportions of the isomers obtained. For *ortho*-substituted phenols the crude alkali hydroxyphenyl sulphate was decomposed without previous removal of unchanged material as described by Baker and Brown (*loc. cit.*), after which the products were extracted with an organic solvent and fractionated *in vacuo*. Extraction of unchanged material before decomposition of the sulphate proved necessary, however, with *m*-substituted phenols, as separation of the latter from their oxidation products could not be effected by distillation. Carboxylic acids were esterified before fractionation.

The catechols and quinols were separated by fractionation under reduced pressure. Purification of the catechols by redistillation proved more convenient than the method employing their lead salts which was, in any case, best avoided when working with easily hydrolysed esters.

Experimental.

Both potassium and ammonium persulphate were employed for the oxidations, which were carried out essentially as described by Baker and Brown (*loc. cit.*). All distillations were carried out using a nitrogen leak. The identities of the oxidation products were checked in all instances by mixed m. p. determinations with authentic materials.

Gentisic and Catechuic Acids.—(*a*) Crude gentisic acid (900 g.) was heated under reflux for 8—10 hours with methanol (11·7 l.) containing concentrated sulphuric acid (180 ml.). Three-fifths of the methanol were distilled off and the residue was poured into water (*ca.* 10 l.). The product was extracted with ether (4 × 1·5 l.) and separated into fractions (i) b. p. 55—65°/0·5 mm. (175 g.), (ii) b. p. 65—95°/0·5 mm. (*ca.* 120 g.), and (iii) b. p. 120—130°/0·5 mm. (475 g.), by distillation under reduced pressure employing a 6-inch " bubble and pear " column.

Fraction (i) consisted of methyl salicylate. Fraction (iii) was immediately crystallised from chloroform–light petroleum (b. p. 40—60°), yielding methyl gentisate (435 g.), m. p. 86—87°. The mother-liquors were freed from solvent and added to fraction (ii) which was redistilled, material of b. p. 60—65°/0·4 mm. (*ca.* 120 g.) being collected. Crystallisation from chloroform–light petroleum (b. p. 40—60°) (1 : 3) gave methyl catechuate (78 g.) in stout shining blades, m. p. 78—80° (Found: C, 57·0; H, 5·0. Calc. for $C_8H_8O_4$: C, 57·1; H, 4·8%).

The ratio of gentisate : catechuate was approx. 6 : 1.

(*b*) Potassium persulphate (200 g.) was slowly added, with stirring, to *m*-hydroxybenzoic acid (100 g.) dissolved in a cold solution of sodium hydroxide (138 g.) in water (3075 ml.). After 48 hours at room temperature the mixture was acidified to Congo-red with 10*N*-sulphuric and filtered, and unchanged acid extracted with ether. The aqueous liquors were heated to 90° for 1 hour, cooled, acidified with concentrated hydrochloric acid (50 ml.), and extracted thoroughly with ether. Esterification of the brown semi-crystalline product (42 g.), followed by distillation under reduced pressure, gave fractions (i), b. p. 75—95°/0·4 mm. (800 mg.), identified as methyl catechuate (530 mg.), m. p. 78—79° (Found: C, 57·3; H, 4·8%), and (ii), b. p. 95—125°/0·4 mm., which proved to be methyl gentisate (11·2 g.) (*p*/*o* ratio = 20 : 1).

Nitroquinol and 3-Nitrocatechol.—*o*-Nitrophenol (300 g.) was oxidised (cf. Elbs, *loc. cit.*) in sodium hydroxide solution (400 g. in 6 l. of water) with ammonium persulphate (500 g.) for 40 hours at room temperature. The liquors were then acidified to Congo-red and filtered, and the filtrate was heated at 80° for 30 minutes. The product was extracted with ethyl acetate (3 × 1·5 l.), the solvent removed, and the residue extracted with ether (3 × 1·5 l.). The material so obtained was thoroughly extracted with boiling light petroleum (b. p. 60—80°), the combined extracts were freed from solvent, and the residue was distilled as above. 3-Nitrocatechol, b. p. 80—95°/0·7 mm. (7·5 g.), was obtained, and after purification from light petroleum, formed yellow needles (7·1 g.), m. p. 86° (Found: C, 46·8; H, 3·3; N, 9·4. Calc. for $C_6H_5O_4N$: C, 46·5; H, 3·2; N, 9·0%).

The fraction insoluble in light petroleum was added to the high-boiling residue and distillation continued without a column. Nitroquinol was obtained, having b. p. 95—120°/0·5 mm. and forming red rhombs (43—44 g.), m. p. 132—133°, from boiling water (*p*/*o* ratio = 6 : 1).

Quinol and Catechol.—The black semi-crystalline oil (*ca.* 40 g.) obtained by oxidising phenol was heated under reflux with benzene for 10 minutes and allowed to cool; crude quinol (22 g.) separated and was removed. The benzene liquors were evaporated to dryness, and the residue was dissolved in 50% aqueous alcohol (100 ml.) (distilled water employed throughout) and treated with an excess of an aqueous concentrated solution of lead acetate. The flocculent white precipitate was coagulated by heating the mixture on a water-bath for 15 minutes. It was then collected and washed with a little alcohol, and the wet, uncaked product dissolved in hot aqueous acetic acid (40 ml. of 1 : 1), diluted with water (200 ml.), and extracted with ether (3 × 150 ml.). The brown material so obtained gave catechol (2·0 g.), b. p. 100—230°, on distillation. After purification from benzene it formed shining plates (1·85 g.), m. p. 104—106° (Found: C, 65·2; H, 5·6. Calc. for $C_6H_6O_2$: C, 65·5; H, 5·5%) (*p*/*o* ratio = 10 : 1).

Chloroquinol and 3-Chlorocatechol.—Distillation (column) of the black oily product obtained by oxidising *o*-chlorophenol (385 g.) gave fractions (i), b. p. 70—100°/1 mm. (16·5 g.), and (ii), b. p. 100—120°/1 mm. (129 g.). Redistillation of fraction (i) gave 3-chlorocatechol (11—12 g.), b. p. 65—67°/0·5 mm., crystallising from light petroleum (b. p. 40—60°) in white flakes, m. p. 46—47° (Found: C, 50·1; H, 3·4; Cl, 24·7. Calc. for $C_6H_5O_2Cl$: C, 49·8; H, 3·5; Cl, 24·5%) (*p*/*o* ratio = 10 : 1). Crystallisation of fraction (ii) from the chloroform gave chloroquinol (110 g.), shining white plates, m. p. 103°.

Gentisaldehyde and Catechualdehyde.—(*a*) Oxidation of salicylaldehyde (600 g.) gave a black tarry oxidation product (250 g.) which was shaken twice with boiling benzene (2 × 1·4 l.), the supernatant liquors being decanted each time. The combined benzene extracts (charcoal) were concentrated to *ca.* 1·2 l., gentisaldehyde (170 g.) separating on cooling, in feathery yellow plates, m. p. 98—99°. The mother-liquors were taken to dryness, and the residue was distilled (column) under reduced pressure, the fraction of b. p. 60—85°/0·2 mm. being collected. Crystallisation of this fraction from benzene–light petroleum (b. p. 40—60°) gave catechualdehyde (24—27 g.) in lemon-yellow needles, m. p. 104—105° (Found: C, 60·2; H, 4·5. Calc. for $C_7H_6O_3$: C, 60·9; H, 4·4%). A further quantity (1·5 g.) was isolated from the mother-liquors by the lead-salt technique. Gentisaldehyde (10 g.) (fraction, b. p. 85—115°/0·2 mm.) was obtained from the residue in the distillation flask (*p*/*o* ratio = 7 : 1).

(*b*) *m*-Hydroxybensaldehyde (100 g.) was oxidised as described by Hodgson and Beard (*loc. cit.*) and the product isolated with ether and distilled under reduced pressure (column). Catechualdehyde, b. p. 70—80°/0·2 mm., distilled (Found: C, 61·1; H, 4·6. Calc. for $C_7H_6O_3$: C, 60·9; H, 4·4%), followed by the main bulk of the gentisaldehyde, b. p. 85—110°/0·2 mm. These were purified as before (800 mg. and 18 g.) (*p*/*o* ratio = 22 : 1).

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481. *Ion-exchange and Ion-sieve Processes in Crystalline Zeolites.*

By R. M. BARRER.

Ion-exchange properties of analcite and chabazite have been investigated and compared by using percolation, hydrothermal, vapour-phase, and melt methods. Analcite interchanged Na^+ freely for K^+, NH_4^+, Ag^+, Tl^+, and Rb^+, but gave slight or negligible exchange of Na^+ for Li^+, Ca^+, Mg^{++}, Ca^{++}, or Ba^{++}. There was a complete ion-sieve effect between Rb^+ (radius 1·48 A.) and Cs (radius 1·65 A.). Chabazite on the other hand exchanged freely among the ions Li^+, Na^+, K^+, NH_4^+, Rb^+, Ca^+, Ag^+, Tl^+, Ca^{++}, Sr^{++}, and Ba^{++}. Of ions tried only Mg^{++} failed to exchange.

The extent of hydration of ion-exchanged forms was determined, and also the extent to which lattice modification through exchange could be detected by *X*-ray powder photography. Minor changes from cubic to near tetragonal were often noted with ion-exchange analcites, but with chabazite there were no significant alterations. The ease of exchange is discussed in terms of the openness and character of the aluminosilicate framework; cationic radius and valency; ion-hydration and other factors. Recrystallisation was often found to supersede ion exchange, and the formation of several species including pollucite was examined.

CHABAZITE $[(Ca,Na_2)O,Al_2O_3,4SiO_2,6H_2O]$, mordenite $[(Na_2,Ca,K_2)O,Al_2O_3,10SiO_2,6\frac{1}{2}H_2O]$, and analcite $(Na_2O,Al_2O_3,4SiO_2,2H_2O)$ form a triad of crystals permeated by interstitial channels which become progressively less open in the order given. The character and the dimensions of these channels have been closely studied by molecular-sieve methods (Barrer and Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 195, 206; Barrer, *J. Soc. Chem. Ind.*, 1945, **64**, 130T, 132T; Barrer and Belchetz, *ibid.*, 1945, **64**, 131T; Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555; Barrer and Riley, *J.*, 1948, 133). Some time ago an investigation was commenced of the ion-exchange properties of the three minerals, with a view to the production of modified molecular-sieve sorbents, and the study of ion-sieve behaviour among the species.

Part of this programme has been carried out. Mordenites modified by ion exchange show interesting gradations in molecular-sieve action (within limits set by the character of the

aluminosilicate framework) which lead to new possibilities of separating molecular mixtures (Barrer, *Trans. Faraday Soc.*, 1949, **45**, 363). A similar study of the effects of exchange on sorption equilibria has been made, by using some of the ion-exchange forms of chabazite to be described later (Barrer and Riley, *Trans. Faraday Soc.*, in the press). Ion-exchange processes involving analcite and chabazite will now be discussed and compared between themselves, and with those of mordenite (Barrer, *J.*, 1948, 2158). These three zeolites differ, as ion-exchange media, from clay minerals and amorphous or gel zeolites in that they are not subject to marked swelling and shrinking during exchange. Because they are based on non-shrinking aluminosilicate frameworks they are potentially capable of functioning as ion sieves just as they function as molecular sieves.

Previous work on exchange in crystalline zeolites is fragmentary. It includes, *inter alia*, studies on mordenite (Barrer, *J.*, 1948, 2158) and chabazite (Wiegener and Cernescu, *Trans. Internat. Congr. Soil Sci.*, 3rd Conf. Oxford, 1935, III, 5). Zoch (*Chem. Erde*, 1914, **1**, 219) has made measurements on several zeolites, finding the ease of entry of the ammonium ion in the order chabazite and stilbite > heulandite > harmotome > scolecite, and Gans (*Jahresb. Preuss. Geol. Landesanstalt, Berlin*, 1905, **26**, 188) had previously noted that chabazite, heulandite, and stilbite underwent exchange more readily than did analcite and natrolite. Clark and Steiger (*Amer. J. Sci.*, 1902, **13**, 27; *Z. anorg. Chem.*, 1902, **29**, 338; *U.S. Geol. Survey Bull.*, 1902, 207), Steiger (*Amer. J. Sci.*, 1902, **14**, 31), and Hey (*Min. Mag.*, 1930, **22**, 422; 1932, **23**, 51, 243; 1933, **23**, 421; 1934, **23**, 483; 1936, **24**, 227) have also made observations of ion exchange in a variety of crystalline zeolites. These data are difficult to compare. The crystal-chemical characters among the zeolites used are diverse; fibrous, laminar and robust framework crystals have all been used. Close comparisons like that now made between analcite and chabazite are essential for an understanding of ion exchange, and are a necessary preliminary to quantitative measurements suitable for testing and developing theories of ion exchange and of solid-state reactions.

Experimental.

Materials.—The chabazite crystals were naturally occurring white crystals from Kyogle, N.S.W., Australia, and pink crystals of Canadian origin. They were freed by hand picking from any rock matrix and ground before being used in ion-exchange studies. Analcite was grown hydrothermally as spheroidal and ikositetrahedral crystals small enough to be used as a rule without further grinding. They were formed by treating gels of approximate composition $Na_2O.Al_2O_3.4SiO_2.xH_2O$ with distilled water at ~200° in steel autoclaves (cf. Barrer, *J.*, 1948, 127, 2158; Faraday Soc. Discussion, No. 5, 1949, p. 326). The yields of analcite approached 100%.

The salts used were chlorides, carbonates, nitrates, nitrites, or sulphates of calcium, strontium, barium, lithium, sodium, silver, potassium, ammonium, thallium, rubidium, and cæsium. Where possible they were of AnalaR quality.

Ion-exchange Methods.—Four procedures for effecting ion exchange were employed: percolation, hydrothermal, fusion, and vapour-phase methods. Percolation is a comparatively mild technique, being confined as a rule to low temperatures (≤100°). Hydrothermal exchange reactions carried out in steel autoclaves were most commonly studied in the temperature range 150° to 310°. The autoclaves had about 20-c.c. capacity. 1—2 G. of powdered zeolite crystals were mixed with an excess of the exchanging salt, placed in the autoclave with 5—15 c.c. of water, and heated for periods between 12 hours and 5 days. The products were carefully washed free from entrained salts, and sometimes hydrothermally extracted with distilled water. They were then dried and stored.

Exchange by the fusion method, *i.e.*, by use of molten salts, required the m. p. of the salt to be low enough to eliminate danger of lattice collapse in the zeolite at the reaction temperature. Barium nitrite (m. p. 217°) was used successfully to introduce barium into chabazite,* and lithium nitrate (m. p. 255°) was also used in this way. Exchange *via* the vapour phase was limited to the use of ammonium salts and so to the introduction of ammonium ions, but the method was often remarkably efficient.† The method was used at 208°, 248°, 340°, and 350°, and easily produced NH_4-analcite, -mordenite, and -chabazite. Both ammonium chloride and zeolite crystals were first outgassed to remove water and so prevent development of a high pressure of water vapour at the experimental temperature. Reaction was carried out in sealed glass tubes and, as before, all products were after reaction carefully freed from entrained and occluded salt.

Optical and X-Ray Examination of Products.—The crystalline reaction products were examined with a Leitz polarising microscope. Crystal form, birefringence, and refractive indices were observed normally in white light, but sometimes in sodium light. The optical method was very useful in demonstrating homogeneity or inhomogeneity of the products. *X*-Ray powder photographs were taken by using Hilger HRX equipment with 9-cm. cameras and filtered Cu-$K\alpha$ radiation. Exposures were of 6—8 hours duration. In subsequent measurements of the spacings from powder photograph intensities of the diffraction arcs were at the same time estimated visually. The *X*-ray method at once established the

* Hydrothermal exchange with barium chloride was equally successful.

† This procedure appears to have been originated by Clark and Steiger (*loc. cit.*).

close similarity between ion-exchanged forms and the parent mineral, or showed when recrystallisation had occurred.

Chemical Examination of Products.—In a number of reactions the amount of the ion characteristic of the zeolite displaced by exchange into the mother-liquor was carefully determined. This procedure was particularly useful when the ion-exchange products were needed intact for investigation as sorbents or for other purposes. In a further group of these ion-exchange reactions partial chemical analyses of the solids were made. Such analyses were confined to determinations of the cations present and so gave the extent of ion exchange. Both these methods of examination were supplemented by taking *X*-ray powder photographs to demonstrate that no recrystallisation of the aluminosilicate framework had occurred. Such a proof usually renders unnecessary a complete determination of $Al_2O_3 : SiO_2$ ratios. However, in a third group of the exchange products more complete chemical analyses were carried out, including determinations of $Al_2O_3 : SiO_2$ ratios. These analyses confirmed the assumption that in the experimental conditions cation interchange normally occurred without change in the molar ratios of silica to alumina. Standard analytical methods were employed for silicates and for the several cations, although in one or two cases special procedures were used. Ammonium was determined by decomposing the NH_4-zeolite with boiling concentrated aqueous sodium hydroxide and absorbing the ammonia in standard acid. Water was determined by measuring the total loss in weight on ignition (ammonia and water) and then calculating from the NH_4^+ content previously found how much water had also been lost.

Results.—Some of the successful ion-exchange experiments are summarised in Table I. The mildest method used was the percolation procedure, which revealed a marked difference between analcite and chabazite. At 20° and 100° analcite gave, by percolation, no evidence of exchange with magnesium chloride and calcium chloride solutions and only slight exchange with aqueous potassium chloride. On the other hand, even at 20° prolonged percolation of sodium chloride and potassium chloride solutions through chabazite gave extensive exchange; only aqueous magnesium chloride still showed negligible interchange. These results accord with the more open diffusion paths permeating the chabazite crystals, compared with those in analcite, and with the less basigenic character of magnesium than of alkaline-earth and alkali metals.*

The more vigorous methods of effecting exchange (by use of fused salts, ammonium chloride vapour, or hydrothermal treatment) demonstrated further differences between chabazite and analcite. Chabazite readily exchanged with Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Ca^{++}, Sr^{++}, and Ba^{++}. Mordenite (Barrer, *J.*, 1948, 2158) has previously been shown to exchange with Li^+, Na^+, K^+, NH_4^+, Ca^{++}, and Ba^{++}. In each case there was among these ions no critical factor of valency or of ionic radius. Crystals of both species may accommodate both uni- and bi-valent cations. Analcite on the other hand underwent exchange with Na^+, K^+, NH_4^+, Ag^+, Tl^+, and Rb^+; but with Li^+, Cs^+, Ca^{++}, and Ba^{++} interchange occurred only to a limited or negligible extent even under extreme conditions (Table II). The crystal can readily accommodate only univalent cations, but not all univalent ions (see Discussion).

There appears to be one difference between mordenite and chabazite. Chabazite (see Table I) gives evidence of intracrystalline occlusion of salt in one or two instances, in addition to exchange. Mordenite (Barrer, *J.*, 1948, 2158) did not give evidence of this occlusion. This observation is in accordance with the more open channels in chabazite, as determined from its molecular-sieve properties. The channels in chabazite are able to contain simple species such as ammonium chloride in addition to the exchanging cations. The narrower channels in mordenite (and the still narrower ones in analcite) are unable to accommodate such species.

Recrystallisation Reactions.—Recrystallisation reactions additional to exchange were observed with analcite and leucite under appropriate conditions using solutions of potassium hydroxide, sodium hydroxide, sodium fluoride, potassium fluoride, potassium carbonate, sodium carbonate, potassium chloride, sodium chloride, sodium sulphate, barium chloride, barium bromide, lithium chloride, and lithium nitrate. This led to a diversity of crystalline aluminosilicates and shows that analcite (or leucite), which is easily made in ~100% yield, is an excellent starting material for syntheses of geochemical as well as chemical significance. These reactions will, however, be described in another paper.

Chabazite also underwent several recrystallisation reactions of considerable interest. As noted in the previous section (see Table II) it was impossible to obtain pollucite (*i.e.*, Cs-analcite) from analcite or leucite by ion exchange, although the three species analcite, leucite, and pollucite are based upon nearly the same aluminosilicate framework (W. H. Taylor, *Repts. Prog. Physics*, 1939, 358) and leucite and analcite are readily interconvertible merely by ion exchange (Na^+,H_2O interchangeable with $K^+ + H_2O$). Nevertheless the much more profound change of chabazite into pollucite occurred readily and unexpectedly under the conditions given in Table III.

Two additional recrystallisation reactions were obtained by using chabazite, each yielding species which have no natural counterparts but have previously been synthesised in the author's laboratory. These minerals were $BaO,Al_2O_3,4SiO_2,nBaCl_2,mH_2O$ ($n = \sim 0{\cdot}66$; $2 < m < 3$) (Barrer, *J.*, 1948, 127) and $Tl_2O,Al_2O_3,4SiO_2$ (H. F. W. Taylor, *J.*, 1949, 1253). The barium mineral was formed occasionally when chabazite was treated at ~200° with water and excess of barium chloride (Table III). This mineral has been grown readily from analcite, leucite, and gels (Barrer, *J.*, 1948, 127), and so its formation from chabazite was not studied further.

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* Magnesium is not normally found in any naturally occurring zeolites. These contain as cations one or more of Na, K, Ca, Sr, and Ba. A similar experiment, in which chabazite was left in contact with aqueous copper sulphate for 18 months, gave no evidence of exchange of Na or Ca for feebly basigenic Cu. Only the *surfaces* of the chabazite crystallites became stained with a green basic copper sulphate.

TABLE I.

Successful exchange reactions with analcite and chabazite.

Ion.	Reaction conditions.	Observations.	Conclusion.
	(a) *Synthetic analcite* (refractive index, n, 1·48$_5$).		
K^+	Analcite given two treatments with aq. KCl (KCl in excess). Each treatment, 1 day at 216°.	*X*-Ray pattern identical with that of natural leucite. $Na_2O : K_2O : Al_2O_3 : SiO_2$ = 0·04 : 0·91 : 1·00 : 3·80; H_2O, 1·51%; n, 1·51.	Exchange nearly complete.
NH_4^+	Analcite heated with NH_4Cl vapour at ~340° for 16 hours.	*X*-Ray pattern rather similar to that of leucite, but with characteristic differences. $(NH_4)_2O$, 11·1; H_2O, 1·5%; Na and Cl, trace. n, 1·52$_5$.	Exchange complete.
Rb^+	Analcite and an equal volume of RbCl heated with 5 c.c. of H_2O for 48 hours at 182°.	*X*-Ray pattern characteristic, based on analcite and pollucite. n, 1·51. H_2O, 1·9%. $Rb_2O : Na_2O$ = 0·85 : 0·15 (molar).	Exchange extensive.
Tl^+	Analcite (1 g.) + Tl_2SO_4 (3 g.) heated with 10 c.c. of H_2O and 2 drops 2N-NaOH at 160° for 5 days.	*X*-Ray pattern identical with that of Tl-analcite crystallised hydrothermally from $Tl_2O,Al_2O_3,4SiO_2$ gel (Taylor, *J.*, 1949, 1253). Diffraction arcs remarkably similar in spacing to Rb-analcite. n, 1·64. H_2O, 0·5; Tl_2O, 49·3%.	Exchange nearly complete.
Ag^+	Analcite (1 g.) + $AgNO_3$ (3 g.) heated with 10 c.c. of H_2O at 160° for 5 days.	*X*-Ray pattern very similar to that of analcite in spacings but not intensity. n, 1·56. H_2O, 8·6; Ag_2O, 20%.	Exchange considerable.
	(b) *Chabazite* (n, 1·48$_5$ *).		
Ba^{++}	Chabazite heated with molten $Ba(NO_3)_2$ at 270° for 44 hours.	Analysis gave $BaO : Al_2O_3 : SiO_2$ = 0·70 : 1·00 : 4·13; also H_2O, 18·9%.†	Exchange considerable.
Sr^{++}	Chabazite heated with aq. $SrCl_2$ (salt in excess) for 2 days at 240°.	*X*-Ray pattern of chabazite with slightly modified intensities. H_2O, 19·3; CaO, 1·5%; SrO, 12·8%. Much occluded $SrCl_2$ removed (before *X*-ray and analysis made) by hydrothermal extraction twice at 248° for 2 days with distilled water. The $SrCl_2$ could not be washed out at 100°.	Exchange considerable.
NH_4^+	(i) 4 G. of chabazite heated with solid NH_4Cl at 206° for 22 hours.	On heating of the product at 350°, copious NH_4Cl evolved from crystals previously thoroughly washed. Thus NH_4Cl had been occluded. 0·120 G. of CaO in mother-liquor from aqueous washings.	Partial exchange.
	(ii) Product from (i) heated with NH_4Cl at 248° for 1 day.	Again copious NH_4Cl evolved at 350° from crystals washed and dried. Washings contained 0·345 g. of CaO. *X*-Ray pattern of chabazite with modified intensities; n, 1·48$_7$.	Exchange nearly complete.
Li^+	Chabazite heated with aq. $LiNO_3$ (salt in excess) for 2 days at 248°. Two treatments given.	Considerable Ca displaced into washings. Chabazite pattern with modified intensities. n, 1·48. H_2O, 14·2; Li_2O, 2·0; CaO, 3·4% (*i.e.*, about 30% exchange).	Exchange partial.
Na^+	Chabazite (<200 mesh) treated with N-NaCl at 20° by continued percolation.	*X*-Ray pattern of chabazite (also similar to that of allied zeolite gmelinite). Initially zeolite gave CaO, 10·1; Na_2O, 2·1%. After exchange it contained 0·5% of CaO, 10·3% of Na_2O and 23·7% of H_2O and had n 1·47$_7$.	Exchange extensive.
K^+	Chabazite (<200 mesh) treated with N-KCl at 20° by continued percolation.	*X*-Ray pattern of chabazite with modified intensities. Initially zeolite gave: CaO, 10·1 and Na_2O, 2·1%. After exchange it contained: CaO, 1·0; $Na_2O + K_2O$, 13·3; H_2O, 18%. n, 1·48.	Exchange extensive.
Rb^+	0·5 G. of chabazite + 1 g. of RbCl + 5 c.c. of H_2O heated for 2 days at 152°.	*X*-Ray pattern of chabazite with some modified intensities. 9% (by wt.) of CaO replaced by Rb_2O. H_2O, 11·2%. n, 1·48.	Exchange extensive.
Cs^+	1 G. of chabazite + 2 g. of CsCl + 5 c.c. of H_2O heated for 4 days at 151°.	*X*-Ray pattern of chabazite with some modified intensities. 5·5% (by wt.) of CaO replaced by Cs_2O. H_2O, 8·2%. n, 1·49$_4$.	Exchange considerable.
Ag^+	1 G. of chabazite + 3 g. of $AgNO_3$ heated with 10 c.c. of H_2O for 5 days at 160°.	*X*-Ray pattern of chabazite with some modified intensities. 11·2% (by wt.) of CaO replaced by Ag_2O. n, 1·49. H_2O, 11·6.%	Exchange complete.

* In all cases mean values only of n are given. Crystals were birefringent, and among ion-exchange forms not always of uniform n.

† The water in barium chabazite was determined on a second preparation made hydrothermally, by using aqueous barium chloride.

TABLE II.

Experiments demonstrating difficulty of exchanging Na^+ *in analcite for* Li^+, Ca^+, Ca^{++}, *or* Ba^{++}.

Ion.	Reaction conditions.	Observations (including analysis).	*X*-Ray pattern (powder photograph).	Conclusion.
Li^+	Analcite heated with molten $LiNO_3$ for 2 days at 290°.*	Na_2O, 13·6; Li_2O, 0·84%.	—	Negligible exchange.
Ba^{++}	Analcite heated with molten $Ba(NO_3)_2$ for 44 hrs. at 270°.	Two expts. gave BaO, 6·5% and negligible, respectively. Some decomposition of analcite.	—	Exchange limited, and some decomposition.
	Analcite heated with aq. $Ba(NO_3)_2$ (salt in excess). Six treatments, each of 2 days, at 200°.	Na_2O (by diff.) : BaO : Al_2O_3 : SiO_2 : H_2O = 0·75 : 0·20 : 1·00 : 3·99 : 2·2.	—	Exchange limited.
	Analcite heated with aq. $Ba(NO_3)_2$ (salt in excess). Six treatments, each of 2 days, at 208°.	Na_2O : BaO : Al_2O_3 : SiO_2 : H_2O = 0·08 : 1·46 : 1·00 : 4·00 : 3·54.	Not analcite or harmotome. Some amorphous.	Decomposition and partial recrystallisation.
	Analcite heated with aq. $Ba(NO_3)_2$ (salt in excess). Four treatments, each of 2½ days, at 310°.	BaO : Al_2O_3 : SiO_2 : H_2O = 0·98 : 1·00 : 4·00 : 2·08.	Largely amorphous.	Decomposition.
	Analcite heated with aq. $Ba(NO_3)_2$ (salt in excess). Five treatments, each of 1 day, at 176°.	Na_2O : BaO : Al_2O_3 : SiO_2 : H_2O = 0·95 : 0·04 : 1·00 : 3·98 : 1·06.	Analcite.	Negligible exchange.
Ca^{++}	Analcite heated with aq. $CaCl_2$ (salt in excess). Five treatments, each of 12 hours, at 200°.	CaO : Al_2O_3 : SiO_2 : H_2O = 0·36 : 1·00 : 4·03 : 1·80.	—	Partial exchange.
	NH_4-analcite prepared as in Table I(a) heated withaq. $Ca(NO_3)_2$ (salt in excess). Four treatments, each of 3 days, at 220°.	$(NH_4)_2O$: CaO : Al_2O_3 : SiO_2 : H_2O = 0·33 : 0·41 : 1·00 : 3·32 : 1·63. Product still zeolitic sorbent to NH_3, but some decomposition.	—	Partial exchange, with some decomposition.
	NH_4-analcite as above heated with excess of $Ca(OH)_2$ + H_2O for 16 hours at 280°.	Material considerably altered.	Weak, and different from that of analcite.	Decomposition and recrystallisation.
Cs^+	NH_4-analcite as above heated with aq. CsCl (salt in excess) at 220° for 3½ days, then for 2 days at 290° with fresh CsCl (1 g.) + H_2O (15 c.c.).	Negligible NH_4^+ displaced into solution. n_D 1·52$_5$ as in parent NH_4-analcite. Cs_2O, 0·23%.	Identical with that of NH_4^+-analcite.	Negligible exchange.
	K-analcite (leucite) of Table I(a) heated with aq. CsCl (salt in excess) for 2 days at 270°.	n_D still 1·50$_5$, similar to that of original leucite.	Identical with that of K-analcite.	Negligible exchange.
	Analcite heated with aq. CsCl (salt in excess) for 2 days at 270°.	n_D 1·49$_0$ (cf. 1·48$_5$ for analcite, and 1·52$_1$ for pollucite).	Identical with that of analcite.	Negligible exchange.

* Hydrothermal methods were also used employing aqueous lithium chloride and lithium nitrate, with an excess of the salt. The analcite, however, recrystallised into several new lithium aluminosilicates.

TABLE III.

Exchange and recrystallisation of chabazite with CsCl, Tl_2SO_4, *and* $BaCl_2$.

Reaction conditions.	Observations.	*X*-Ray pattern.	Conclusion.
Chabazite (1 g.) heated with 2 g. of CsCl and 5 c.c. of H_2O for 4 days at 151° (see Table I).	5·5% of CaO displaced into solution. Optical study showed no growth of pollucite.	Similar to chabazite.	Exchange, but no recrystallisation to pollucite.
Chabazite (1 g.) heated with 1 g. of CsCl and 5 c.c. of H_2O for 2 days at 182°.	6·1% of CaO displaced into solution. n_r ~1·49 but not uniform. Small pollucite crystallites sometimes embedded in surface of larger chabazite crystals.	Similar to chabazite but with several weak pollucite reflections.	Exchange, with some recrystallisation to pollucite.
Chabazite (1 g.) heated with 1 g. of CsCl and 10 c.c. of H_2O for 20 hrs. at 248°. Partial leak caused loss of some water.	Extensive recrystallisation to pollucite, n 1·522. Much CaO displaced into solution.	—	Recrystallisation to pollucite.
Product obtained above at 248° was further heated with 1 g. of CsCl and 10 c.c. of H_2O for 2 days at 248°.	Little further Ca displaced. Crystals, extracted several times with distilled water at 248°, liberated no Ca or Cl into mother-liquor.	Pollucite only.	Recrystallisation to pollucite complete.
Chabazite (1 g.) heated with 3 g. of Tl_2SO_4 and 10 c.c. of H_2O at 160° for 5 days. Twice extracted hydrothermally for 2 days at 220° until free from entrained Tl_2SO_4.	Original chabazite crystals studded with spheroidal crystals. Extensive recrystallisation had occurred.	Pattern of species $Tl_2O,Al_2O_3,4SiO_2$ analogous to those of analcite or leucite, and identical with Tl-analcite.	Recrystallisation to Tl-analcite.
Chabazite (2 g.) heated with excess of $BaCl_2$ and 5 c.c. of H_2O at 208° for 5 days.	Product extracted 5 times with boiling water. Considerable crystal regrowth.	Pattern of a synthetic Ba mineral previously grown hydrothermally.	Recrystallisation to species $BaO,Al_2O_3,4SiO_2$, $nBaCl_2,mH_2O$ (n = ~0·68; $2<m<3$).*

* Barrer, *J.*, 1948, 127.

The thallium mineral was formed as spheroidal crystals when chabazite was heated at 160° with some water and an excess of thallium sulphate (Table III). H. F. W. Taylor (*loc. cit.*) has also grown it from gels, and it has been found that the *X*-ray powder photograph is identical with that of thallium analcite (Table IV). Taylor showed that this mineral can readily be converted into ordinary analcite by the reversible exchange of Na^+,H_2O with $Tl^+ + H_2O$. Accordingly one may at quite low temperatures convert chabazite into analcite by this procedure.

X-Ray Examination of Ion-exchanged Forms.—All ion-exchanged forms of chabazite and analcite were examined by *X*-ray powder photography. Within the closest limits it was possible to establish (i) the structural identity of leucite formed by ion exchange (*i.e.*, K-analcite) and a naturally occurring leucite, (ii) the identity of synthetic pollucite grown by recrystallising chabazite and of a naturally occurring specimen, and (iii) the identity of the mineral $TlAlSi_2O_6$ also grown from chabazite and Tl-analcite formed by ion exchange from analcite (Tables III and IV).

All the chabazite ion-exchanged forms, hydrothermally enriched in Li, Na, Ag, Sr, Ba, K, NH_4, Rb, and Cs, were true chabazites with little or no observable variation in spacings from one another or from the parent chabazite crystals, although showing expected variations in relative intensities of some lines. It may be inferred that the chabazite aluminosilicate framework is open enough and rigid enough to accommodate all cations from Li^+ (the smallest; * r = 0·78 A.) to Cs^+ (the largest; r = 1·65 A.), without significant alteration.

The analcite ion-exchanged forms, although retaining the analcite structure closely, suffered some small adjustments in the aluminosilicate framework. These changes are compatible with the view that the volumes occupied in the lattice by the units H_2O,Na^+ and Cs^+ are practically the same.† Thus both

* Ionic radii are taken from Evans, "Crystal Chemistry," Cambridge Univ. Press, 1938, p. 170. A similar set of radii is given by Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1937, p. 346, and by Slater, "Chemical Physics," McGraw-Hill, 1939, p. 383.

† Pollucite is often formulated as $(Na_2,Cs_2)O,Al_2O_3,4SiO_2,H_2O$, *i.e.*, with half the water present in analcite. This water may be associated with the sodium, in which case a pure Cs-pollucite would be anhydrous; or it may be present in vacant sites in the crystal. W. H. Taylor (*Z. Kristall.*, 1930, **74**, 1) states that there are 24 sites per unit cell in analcite, occupied by only 16 Na^+ ions, and in pollucite which is isostructural with analcite an identical situation must arise. There are thus just enough vacant sites for water molecules to give the above formula; but these water molecules would *not* be associated with the Cs^+ ions. Moisture determination on a synthetic pollucite derived by recrystallising chabazite was not conclusive owing to the presence of a certain amount of the highly hydrated parent chabazite.

TABLE IV.

Identity of some natural and synthetic species.

Natural leucite.*		Synthetic leucite.		Natural pollucite.		Synthetic pollucite.		$Tl_2O.Al_2O_3.4SiO_2$, prepd. by recrystallisation from chabazite.		$Tl_2O.Al_2O_3.4SiO_2$, by ion-exchange from analcite.	
Spacing.	*I.*†	Spacing.	*I.*	Spacing.	*I.*	Spacing.	*I.*	Spacing.	*I.*	Spacing.	*I.*
5·37	s	5·40	ms	3·66	ms	3·65	ms	5·59	s	5·54	s
4·72	vw	4·72	vvw	3·41	s	3·41	s	3·63	vs	3·60	vs
3·40	vs	3·40	vs	$2·90_5$	ms	$2·91_5$	ms	3·35	vs	3·35	vs
3·23	vs	3·23	vs	$2·60_5$	vw	$2·66_5$	vvw	3·20	vw	—	—
$3·03_5$	vw	$3·04_5$	vvw	$2·47_5$	vw	$2·49_5$	vvw	3·00	vw	2·98	vw
$2·88_5$	s	$2·90_5$	s	$2·40_5$	ms	$2·40_5$	m	$2·87_5$	s	$2·86_7$	s
$2·81_5$	s	$2·80_5$	s	2·215	ms	2·209	m	2·651	vw	2·651	vw
$2·60_4$	mw	$2·62_5$	m	2·010	w	2·012	vw	2·446	w	2·431	vw
$2·45_5$	vvw	$2·45_5$	vw	1·969	w	1·974	vvw	2·391	ms	2·378	ms
$2·33_5$	ms	$2·33_5$	ms	1·905	vvw	—	—	2·175	m	2·163	ms
—	—	$2·27_5$	vvw	1·853	ms	1·858	m	1·978	w	1·966	w
2·112	m	2·112	m	1·730	s	1·730	ms	1·936	w	1·933	w
2·045	vw	2·036	vvw	1·699	w	1·701	vw	1·843	w	—	—
1·967	vw	—	—	—	—	1·628	vvw	1·812	m	1·810	m
1·913	w	1·908	vvw	—	—	1·887	vvw	1·726	mw	1·712	w
1·836	w	1·846	vvw	—	—	1·533	w	1·688	m	1·688	m
1·775	m	1·775	w	1·526	mw	1·523	w	1·664	vw	1·662	vw
1·716	m	1·717	w	1·469	w	1·473	vw	1·612	w	1·613	w
1·654	ms	1·654	ms	1·447	w	—	—	—	—	1·552	vw
1·623	w	1·621	w	—	—	1·410	vw	1·521	w	1·522	w
1·575	mw	1·583	w	1·349	mw	1·351	w	1·492	w	1·497	w
1·528	m	1·526	w	1·299	mw	1·303	w	1·460	w	1·457	vvw
1·476	m	1·478	w	1·279	vvw	—	—	1·440	vw	1·433	vvw
1·438	vw	1·442	vw	1·253	vw	1·256	vvw	1·381	vw	1·389	vw
1·406	w	1·410	vw	1·216	w	1·215	w	—	—	1·364	vvw
1·372	mw	1·374	w	1·177	w	1·180	w				
1·355	mw	1·355	w	1·160	vvw	—	—				
1·319	w	1·319	w	1·136	vw	1·139	vvw				
1·295	mw	1·295	w	1·114	w	1·120	w				
1·269	w	1·268	vw	1·037	vw	—	—				
1·242	m	1·246	w	—	—	0·972	vw				
1·201	vw	1·201	w	0·951	w	0·953	w				
1·163	vw	1·163	w								
1·140	vw	—	—								
1·120	vw	1·126	vvw								
1·084	vvw	—	—								
1·064	vvw	1·061	vvw								
0·996	vvw	—	—								
0·984	vvw	—	—								
0·968	vvw	—	—								
0·949	vvw	0·949	vvw								

* Supplied by Prof. Hawkes, Bedford College, Regent's Park, London, N.W.1.

† *I* = Intensity.

TABLE V.

Water content of ion-exchanged forms.

	H_2O found, %.	H_2O, %, calc. for M_2O(or MO).$Al_2O_3.4SiO_2.mH_2O$ (m = 6 for chabazite and 2 for analcite).	No. of moles of H_2O per unit of M_2O(or MO).$Al_2O_3.4SiO_2$.
Chabazites rich in			
Ca	19·8	21·4	5·6
Sr	19·4	19·3	6·0
Ba	18·9	17·9	6·3
Na	23·7	21·1	6·7
K	18·0	19·8	5·5
Ag	11·6	15·8	4·4
Rb	11·2	17·0	4·0
Li	14·2	22·5	3·8
Cs	8·2	14·8	3·3
Analcites rich in			
Na	8·1	8·2	2·0
Ag	8·6	5·9	2·9
K	1·5	7·6	0·40
NH_4	1·5	8·4	0·36
Tl	0·3	4·4	0·23
Rb	1·9	6·4	0·60

analcite and pollucite gave cubic unit cells with $a = 13{\cdot}6_1$ and $13{\cdot}6_7$ A. for analcite (determinations on two different synthetic specimens) and $a = 13{\cdot}6_4$ A. for pollucite. W. H. Taylor (*Z. Kristall.*, 1930, **74**, 1) gives $a = 13{\cdot}67 \pm 0{\cdot}04$ A. in the case of analcite. It was further found that Ag–analcite prepared hydrothermally was hydrated, like Na-analcite (Table V), and gave a cubic unit cell with $a = 13{\cdot}7$ A. This would be expected since the units H_2O,Na^+ and H_2O,Ag^+ should have similar volumes (for Na^+, $r = 0{\cdot}98$ and for Ag^+, 1·13 A.). However, K-, NH_4-, Rb-, and Tl-analcites proved to be anhydrous so that the increased ionic radii make the units H_2O,M^+ (where $M^+ = K^+$, NH_4^+, Rb^+, or Tl^+) too large to occupy the interstices which previously contained H_2O,Na^+, H_2O,Ag^+, or anhydrous Cs^+. The relevant ionic radii are: K^+, 1·33; NH_4^+, 1·43; Rb^+, 1·48; Tl^+, 1·49; and Cs^+, 1·65 A. On the other hand, the *unhydrated* ions K^+, NH_4^+, Rb^+, and Tl^+ do not fully occupy the interstices, whereas the larger Cs^+ does. From the powder photographs one observed slight distortion in K-, NH_4-, Rb-, and Tl-analcites which transformed the crystals, by a minor contraction of the *a*-axis and expansion of the *c*-axis, from cubic into approximately tetragonal forms, with an axial ratio c/a slightly greater than unity. Tl^+ and Rb^+ have nearly identical radii, and it was notable that the spacings corresponding to their powder photographs were almost indistinguishable.

The results thus interpreted indicate a smaller interstitial volume associated with each cation site in analcite than in chabazite. This conclusion was supported in another decisive way. Li-, Ba-, and NH_4-chabazites were investigated as sorbents and shown, like the parent chabazite crystals, to have excellent sorptive properties towards small molecules.* Among the analcites, however, dehydrated synthetic Na-analcite was found to sorb small polar gases only (H_2O, NH_3, HCl), and the sorptive properties of K- and NH_4-analcites were negligible.

Interstitial Water.—The water contents of the various ion-exchanged crystals were determined as total water (in addition to intracrystalline water there may thus be small amounts of adsorbed water). The results are summarised in Table V. Col. 2 gives the total water content found, col. 3 that calculated for a formula $M_2O(\text{or } MO),Al_2O_3,4SiO_2,6H_2O$ on the assumption of complete exchange, and col. 4 gives the number, *n*, of moles of water per unit $M_2O(\text{or } MO),Al_2O_3,4SiO_2$.

Among the analcites, only the Na^+- and Ag^+-ion-exchanged forms are hydrated. As noted in the previous section, the anhydrous character of the other ion-exchanged forms depends more on the small interstitial volume available than on the affinity between water molecules and ions. On the other hand, owing to the greater available interstitial volume in chabazite, all the ion-exchanged forms are hydrated, and there are several water molecules per cation. The extent of hydration under ordinary conditions of humidity of the atmosphere is compatible with the hydration series of the ions.† Full saturation of the crystals corresponds to six water molecules per cation for Ca^{++}-, Sr^{++}-, and Ba^{++}-chabazites, and three water molecules per ion for at least some univalent cations. If as is considered for some of the fibrous zeolites (W. H. Taylor, *Proc. Roy. Soc.*, 1934, *A*, **145**, 80) the water molecules are grouped directly around the cation, there would be a co-ordination shell of six water molecules per bivalent cation, and of three for a univalent cation. In the limited interstitial environment the co-ordination number 6 seems high, and some water molecules may be displaced away from the first hydration shell into vacant sites. Vacant sites can arise in a crystal in which all positions are occupied by univalent ions when these ions are replaced by half their number of bivalent ions. Another aspect of this replacement is considered below (see Discussion).

Discussion.

Reference has been made (p. 2344) to the observation that although analcite, leucite, and pollucite are based on virtually the same aluminosilicate framework, so that analcite and leucite are readily interconvertible simply by ion interchange (Na^+,H_2O interchangeable with $K^+ + H_2O$), nevertheless neither analcite nor leucite will give pollucite by ion exchange. This is a very good example of ion-sieve action. The ions Na^+, Ag^+, K^+, NH_4^+, Tl^+, and Rb^+, with radii 0·98, 1·13, 1·33, 1·43, 1·49, and 1·46 A. respectively, can diffuse into analcite crystals, but Cs^+ (radius = 1·65 A.) cannot. It follows that Na^+–K^+ exchanges of the above type (*i.e.*, analcite $\rightleftharpoons$ leucite) are easily established, but that the Na^+–Cs^+ and K^+–Cs^+ equilibria cannot be established. In the synthesis of pollucite the Cs^+ cations are accordingly locked within the crystal once and for all during its growth and can be released only by its recrystallisation or decomposition. The correctness of this view was further demonstrated by hydrothermal treatment of powdered pollucite with a series of saline solutions (sodium chloride, lithium chloride, sodium carbonate, ammonium chloride, and barium chloride) at high temperatures (~300°).‡ These treatments effected no observable change in the refractive index of the pollucite such as ion exchange normally produces (cf., for example, Table I*a*).

* This work, carried out with Dr. Riley, is described elsewhere (*Trans. Faraday Soc.*, in the press).

† The energy of interaction of a permanent dipole of moment μ with a charge ϵ is $E_1 = -\mu\epsilon\cos\theta/r^2$. Taking the diameter of a water molecule as 2·8 A. and a fixed orientation, θ, of the dipole axis relative to the line joining the charge and the centre of the dipole, and assuming that r = the radius of a dipolar molecule + the radius of the cation, one finds that E_1 decreases in the sequence $Ca^{++} > Sr^{++} > Ba^{++} > Li^+ > Na^+ > Ag^+ > K^+ > NH_4^+ > Rb^+ > Cs^+$. Again, for the polarisation energy of the molecule by the cation, $E_2 = -\alpha\epsilon^2/r^4$, where α is the polarisability of the molecule, one finds the same sequence in the ion series. With the exception of Li^+, this series recalls the extent of hydration in ion-exchange chabazites shown in Table V.

‡ Those treatments were carried out by Dr. H. F. W. Taylor.

Another aspect of the ion-sieve effect may help to explain the difficulty of obtaining Ca- and Ba-rich analcites (Table II). In analcite crystals, the interstitial channels suffer periodic restrictions sufficient to prevent diffusion of cæsium. In these periodically restricted channels the replacement of uni- by bi-valent ions is shown by the change from Fig. 1 to Fig. 2, which give schematically the charge distributions. The bivalent cations cannot easily occupy positions at the restrictions in the channels for steric reasons; on the other hand, their presence in only half of the sites normal for univalent cations leads to a state of local disbalance of cationic and anionic charge. Since neither configuration is then very stable, exchange of uni- for bi-valent cations in analcite will be limited in extent. On the other hand, in chabazite and mordenite the restrictions in the interstitial channels are less marked, as demonstrated by their sorptive and molecular-sieve behaviour (cf. Barrer, *Ann. Reports*, **1944**, **41**, 31, for a summary of these properties). There is now adequate room for bivalent cations to occupy intermediate positions along the channel, the configuration shown in Fig. 3 becoming that in Fig. 4 when univalent are replaced by bivalent cations; local neutralisation of anionic charge is much more nearly effected, and exchange proceeds easily either way.

FIG. 1. FIG. 2.

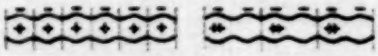
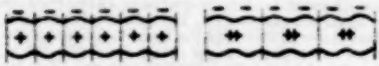


FIG. 3. FIG. 4.



Local balance or disbalance of anionic and cationic charges shown diagrammatically, in relation to interstitial channel dimensions.

Other factors are also considered to contribute to the extent of exchange. Very small ions such as Li^+ and Mg^{++} do not interchange freely, but this may be associated with a high energy of hydration in solution and with changes in the degree of hydration during exchange.* Wiegener and Cernescu (*loc. cit.*) who compared the behaviour of Li^+, Na^+, K^+, Rb^+, and Cs^+ in ion exchange in chabazite, emphasised the hydration factor, which they considered to be connected with the ease of entry (stated to be in the order $K^+ > Na^+ > Li^+$). However, the direction in which the hydration factor would operate is not certain; much must depend upon the ion being displaced.

The basigenic character of the element is also of significance. Magnesium is comparatively weakly basigenic and its salts are hydrolysed fairly easily to basic salts. Hydrolysis may be augmented under hydrothermal conditions. Silver ions, on the other hand, are not strongly hydrated but the salts are not hydrolysed under comparable conditions. Silver, in fact, replaces other cations in chabazite and analcite surprisingly easily, but magnesium does not do so. It is thus clear that a diversity of factors may operate in controlling ion exchange. The factor of swelling and shrinking present in clay minerals and in gel exchangers has, however, been largely avoided in the present study by using crystals where shrinking and swelling are negligible, and these results may be to this extent simplified.

MARISCHAL COLLEGE, ABERDEEN UNIVERSITY. [*Received, May 5th*, 1950.]

* Hydration cannot, however, control exchanges occurring from a melt, and the same difficulty arises when Na^+ is replaced by Li^+ by this method (Table II) as in hydrothermal exchange. Hydrolysis also cannot affect the results of exchange by fusion.

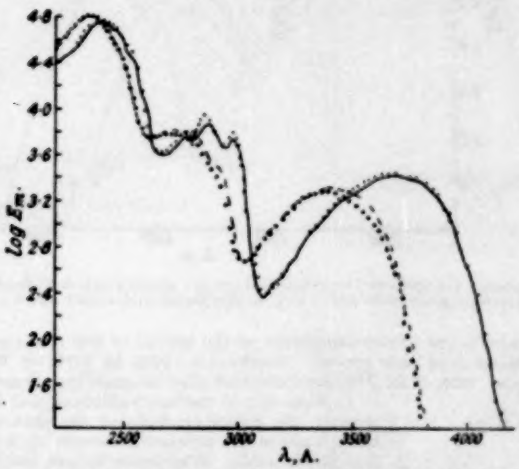
482. *Ultra-violet Spectrum and Constitution of 3-Hydroxy-2-naphthoic Acid and Related Compounds.*

By Ernst D. Bergmann, Y. Hirshberg, and S. Pinchas.

The ultra-violet absorption spectra of this acid and its methyl ester give indications of hydrogen-bonding in the acid, and this is supported by infra-red spectra. The ultra-violet spectra of the *O*-methyl derivatives of the above and of salicylic acid and its ester and also of certain acetylnaphthols are recorded.

It has long been known that 3-hydroxy-2-naphthoic acid (I) and its methyl ester are yellow (Schmidt and Burkard, *Ber.*, 1887, **20**, 2702; Strohbach, *Ber.*, 1901, **34**, 4153; H. Meyer, *Monatsh.*, 1901, **22**, 791), whilst 1-hydroxy-2- and 2-hydroxy-1-naphthoic acid and also

Fig. 1.



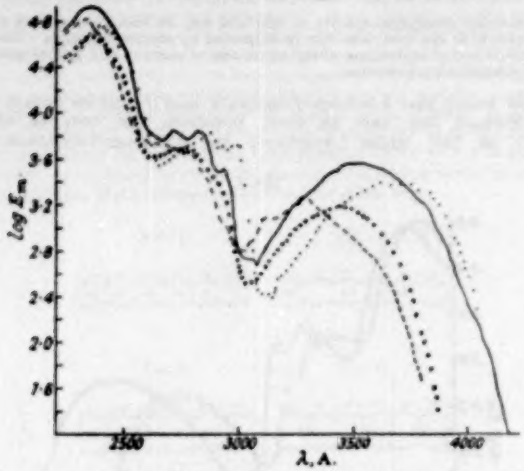
Dioxan solutions of 3-*hydroxy*-2-*naphthoic acid* (——); *methyl* 3-*hydroxy*-2-*naphthoate* (· · ·); 3-*methoxy*-2-*naphthoic acid* (– – –); *methyl* 3-*methoxy*-2-*naphthoate* (× × ×).

3-methoxy-2-naphthoic acid (II) and its methyl ester are colourless. As no theoretical explanation of this somewhat surprising effect appears to have been attempted, an investigation was undertaken. Fig. 1 shows the absorption spectra of dioxan solutions of 3-hydroxy- and 3-methoxy-2-naphthoic acid and of their methyl esters in the ultra-violet (and the visible) region. The spectra of the respective free acids and their methyl esters are identical, but there are visible differences between the 3-hydroxy-compounds on the one hand and the 3-methoxy-derivatives on the other: especially, the maximum at 3700 A. in the spectrum of the hydroxy-acid is shifted into the ultra-violet (3400 A.) upon methylation. It is suggested that this difference is due to the occurrence of hydrogen bonding in the hydroxyl compounds (see below).

A second effect becomes evident if one compares the spectra of the dioxan (Fig. 1) and of the ethyl alcoholic (Fig. 2) solutions of the four compounds. The hydroxylic solvent does not affect the spectra of the two methyl esters, while those of the free acids are somewhat influenced, probably owing to a loose addition of solvent molecules to the carbonyl double bond of the carboxyl group, as is known for aldehydes and ketones (Herold and Wolf, *Z. physikal. Chem.*, 1931, *B*, **12**, 165, 194). It is in keeping with this hypothesis that the influence of the alcohol is much more prominent with 3-hydroxy-2-naphthoic acid than with the 3-methoxy-compound; indeed, there is almost no difference in the position of the "3500-A. band" in the alcoholic solutions of the two compounds. It is reasonable to assume that the solvent competes with the

intramolecular hydrogen bond in the former acid and, thereby, destroys the cause of the difference between the spectra of the two acids.

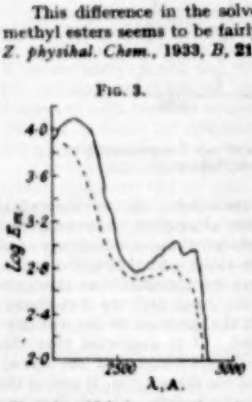
FIG. 2.



Alcoholic solutions of 3-*hydroxy*-2-*naphthoic acid* (——); *methyl* 3-*hydroxy*-2-*naphthoate* (· · · ·); 3-*methoxy*-2-*naphthoic acid* (– – –); *methyl* 3-*methoxy*-2-*naphthoate* (× × ×).

This difference in the solvent-dependency of the spectra of free aromatic acids and their methyl esters seems to be fairly general. Scheibe (*Ber.*, 1926, **59**, 2617; cf. Wolf and Strasser, *Z. physikal. Chem.*, 1933, *B*, **21**, 389) has shown that ethyl benzoate has almost identical spectra in heptane and in methanol solutions, and Fig. 3 and Fig. 4 indicate the differences between the ultra-violet spectra in ethanol and in non-hydroxylic solvents for benzoic and 1- and 2-naphthoic acids. Whereas for benzoic and 2-naphthoic acid, the difference lies more in a decrease in intensity than in a shift of the maxima, on transition to ethanol, yet the effect in the case of 1-naphthoic acid is remarkable inasmuch as the longer band shifts by 140 A. to the ultra-violet in ethanol, as compared with dioxan (the spectra of the two naphthoic acids in hexane solution have been measured by de Laszlo, *Proc. Roy. Soc.*, 1926, *A*, **111**, 355).

FIG. 3.



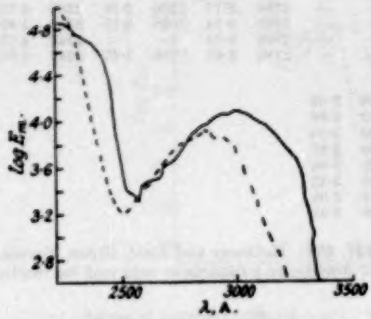
Benzoic acid in isooctane (——) *and alcohol* (– – –).

It is interesting to compare the behaviour of the corresponding phenyl compounds with that of the above naphthalene derivatives. As Fig. 5 shows, salicylic acid and methyl salicylate have the same absorption spectrum in non-hydroxylic solvents, and the same holds true for *o*-methoxybenzoic acid and its methyl ester. The longer absorption band of the hydroxy-compounds lies again nearer to the visible than that of the corresponding methoxy-derivatives. Comparison with Fig. 6, in which the analogous absorption spectra in ethyl alcohol are collated, proves that in this case also, the methyl esters are not affected by the change of solvent, whilst the free acids become more transparent in the hydroxylic solvent. However, the difference is smaller than in the naphthalene series [cf. Ley and v. Engelhardt, *Z. physikal. Chem.*, 1910, **74**, 43; Ley, *Z. wiss. Phot.*, 1919, **18**, 177 (*Centr.*, 1919, I, 947); Gibbs and Pratt, *Centr.*, 1913, II, 1045; Magini, *J. Chim. physique*, 1904, **2**, 403].

The spectrographic data are summarized in Table I.

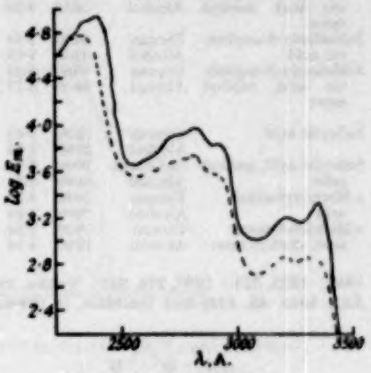
In order to verify the hypothesis offered, the infra-red absorption of methyl salicylate and methyl 3-hydroxy-2-naphthoate was studied. In carbon tetrachloride solution, and at a concentration of about 0·1 g./c.c., they showed an absorption at 3192 and 3245 cm.$^{-1}$, respectively, and with approximately the same intensity. This indicates strong hydrogen bonding. Buswell,

FIG. 4a.



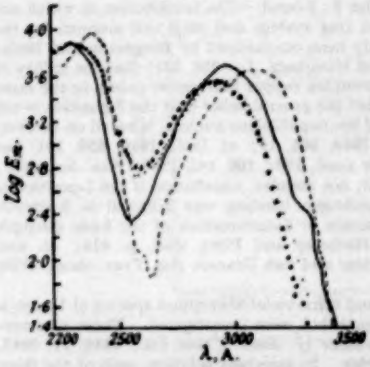
1-*Naphthoic acid in dioxan* (——) *and alcohol* (– – –).

FIG. 4b.



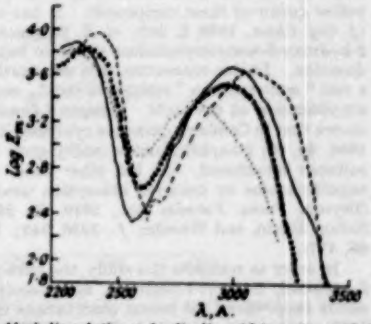
2-*Naphthoic acid in dioxan* (——) *and alcohol* (– – –).

FIG. 5.



Dioxan solutions of salicylic acid (——); *methyl salicylate* (– – –); *o-methoxybenzoic acid* (· · · ·); *methyl o-methoxybenzoate* (× × ×).

FIG. 6.



Alcoholic solutions of salicylic acid (——); *methyl salicylate* (– – –); *o-methoxybenzoic acid* (· · · ·) *methyl o-methoxybenzoate* (× × ×).

Deitz, and Rodebush (*J. Chem. Physics*, 1937, **5**, 501) found the hydroxyl absorption in methyl salicylate shifted to about 3350 cm.$^{-1}$ (*cf.* also Davies and Sutherland, *ibid.*, 1938, **6**, 755. For the modified carbonyl frequency, see Gordy, *J. Chem. Physics*, 1940, **8**, 516). The hydrogen bonding in salicylic acid expresses itself equally in the unusually high dissociation constant of that acid (Dippy *et al.*, *J.*, 1937, 1421; Branch and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 2568).

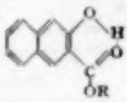
Now, a stable hydrogen-bonded ring implies the presence of a six-membered structure (III) with two conjugated double bonds (Sidgwick and Callow, *J.*, 1924, **125**, 527; W. Baker, *J.*, 1934,

TABLE I.

Ultra-violet absorption maxima of aromatic o-hydroxy-acids and derivatives.

	Solvent.	λ, A.	log $E_{max.}$	λ, A.	log $E_{max.}$	λ, A.	log $E_{max.}$	λ, A.	log $E_{max.}$	λ, A.	log $E_{max.}$
3-Hydroxy-2-naphthoic acid	Dioxan	3680	3·41	2980	3·71	2860	3·87	2760	3·75	2390	4·74
	Alcohol	3280	3·28	—	—	2760	3·74	2660	3·78	2320	4·80
3-Hydroxy-2-naphthoic acid, methyl ester	Dioxan	3660	3·43	2980	3·76	2860	3·92	2760	3·78	2400	4·76
	Alcohol	3640	3·39	2980	3·73	2860	3·87	2760	3·74	2380	4·75
3-Methoxy-2-naphthoic acid	Dioxan	3410	3·28	—	—	2780	3·77	2700	3·78	2350	4·78
	Alcohol	3280	3·28	—	—	2760	3·74	2660	3·75	2320	4·80
3-Methoxy-2-naphthoic acid, methyl ester	Dioxan	3380	3·24	—	—	2690	3·74	—	—	2340	4·76
	Alcohol	3400	3·17	—	—	2780	3·67	2710	3·67	2340	4·65
Salicylic acid	Dioxan	3060	3·63	2370	3·89						
	Alcohol	2980	3·68	2310	3·88						
Salicylic acid, methyl ester	*iso*Octane	3080	3·63	2380	3·98						
	Alcohol	3060	3·64	2380	3·97						
o-Methoxybenzoic acid	Dioxan	2930	3·50	2320	3·84						
	Alcohol	2800	3·40	2260	3·82						
o-Methoxybenzoic acid, methyl ester	Dioxan	2920	3·54	2310	3·84						
	Alcohol	2940	3·54	2340	3·82						

1684; **1935**, 628; **1936**, **274**, 346; *Nature*, 1936, **137**, 236; Hathway and Flett, *Trans. Faraday Soc.*, 1949, **45**, 818) and therefore, in the case of 3-hydroxy-2-naphthoic acid and its methyl

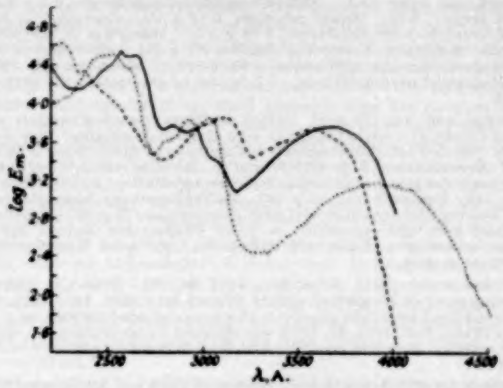
(III.)  (IV.)

ester, unusually large double-bond character of the 2 : 3-bond. The constitution at which one thus arrives, *viz.*, (IV), contains an *ortho*-quinoid ring system and may well account for the yellow colour of these compounds. It has already been emphasized by Bergmann and Berlin (*J. Org. Chem.*, 1939, **3**, 246; cf. E. Bergmann and Hirshberg, *J.*, 1936, 331) that the ability of 2-hydroxy-3-acetylnaphthalene oxime to form a complex copper derivative, points in the same direction. In this connection, it is noteworthy that the general belief that the 3-position is not a real " *ortho*-position " relative to the $C_{(1)}$ atom of the naphthalene nucleus, is based on an oversimplification of the facts. Huisgen (*Annalen*, 1949, **564**, 16; cf. *ibid.*, 1948, **559**, 101) has shown that in Combes's quinoline synthesis (*Compt. rend.*, 1888, **106**, 142, 1536; *Bull. Soc. chim.*, 1888, **49**, 89) 2-naphthylamine readily gives linear, not angular, annellation if the 1-position is suitably substituted. On the other hand, no hydrogen bonding was detected in 3-nitro-2-naphthylamine by infra-red absorption measurements or determination of the basic strength (Bryson, *Trans. Faraday Soc.*, 1949, **45**, 257; Hathway and Flett, *ibid.*, p. 818; cf. also Nolan, Slavin, and Wheeler, *J.*, 1950, 340; Ketelaar and van Dranen, *Rec. Trav. chim.*, 1950, **69**, 477).

In order to complete this study, the infra-red and ultra-violet absorption spectra of 1-acetyl-2-naphthol, 2-acetyl-1-naphthol, and 3-acetyl-2-naphthol were investigated. These measurements supplement the recent observations of Melchior (*J. Amer. Chem. Soc.*, 1949, **71**, 3647, 3651) on the isomeric *ortho*-hydroxynaphthaldehydes. In *iso*octane solution, each of the three hydroxy-ketones shows three absorption bands; the longest one distinguishes the 2 : 3-compound from its isomers; its maximum lies at 3900 A. (as against about 3600 A. for the isomers) (Fig. 7; Table II). In alcoholic solution, too (Fig. 8), there are pronounced differences: the spectrum of the 2 : 3-compound is practically unaffected, that of 1-acetyl-2-naphthol loses its structure without material change in location or intensity of the bands, and that of 2-acetyl-1-naphthol also shows less fine-structure, but a certain increase in the intensity of the longest band. In the infra-red region, 1-acetyl-2-naphthol shows very clearly the shift characteristic of the hydrogen-bonded hydroxyl (at 3360 $cm.^{-1}$), and in both 2-acetyl-1-naphthol and 3-acetyl-2-naphthol the hydroxyl band has merged into the C–H absorption between 3100 and 2900 $cm.^{-1}$. The effect is marked, but it seems that the carbonyl group in these ketones is less responsive to hydrogen bonding than the carbomethoxy-group in the corresponding esters. It may be added that in

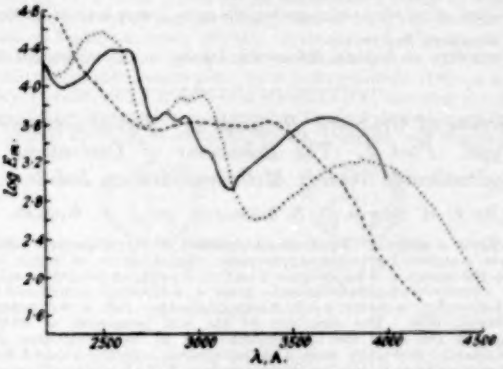
2-hydroxy-1-naphthaldehyde, too, which was studied for comparison, hydrogen bonding is indicated by the shift of the hydroxyl absorption to 3240 cm.$^{-1}$.

FIG. 7.



isoOctane solutions of 2-*acetyl*-1-*naphthol* (——); 1-*acetyl*-2-*naphthol* (– – –); 3-*acetyl*-2-*naphthol* (· · · ·).

FIG. 8.



Alcoholic solutions of 2-*acetyl*-1-*naphthol* (——); 1-*acetyl*-2-*naphthol* (– – –); 3-*acetyl*-2-*naphthol* (· · · ·).

TABLE II.

Ultra-violet absorption maxima of the o-*acetylnaphthols.*

	Solvent.	λ, A.	log E_m.	λ, A.	log E_m.	λ, A.	log E_m.	λ, A.	log E_m.
2-Hydroxy-3-acetyl-	*iso*Octane	2500	4·54	2920	3·86	3020	3·88	3860	3·20
	Alcohol	2500	4·46	2940	3·80	3040	3·82	3900	3·18
2-Hydroxy-1-acetyl-	*iso*Octane	2250	4·60	—	—	3120	3·85	3580	3·73
	Alcohol	2270	4·71	—	—	2990	3·60	3370	3·58
1-Hydroxy-2-acetyl-	*iso*Octane	2560	4·58	2840	3·78 *	2950	3·75	3660	3·76
	Alcohol	2580	4·39	2840	3·71 †	2940	3·68	3660	3·66

* This maximum is accompanied by two less developed ones [2640 A. (4·50) and 2950 A. (3·75)].
† Slight maximum at 2640 A. (4·38).

Experimental.

The ultra-violet absorption spectra were measured by means of a Beckman spectrophotometer, the infra-red spectra by means of a Perkin–Elmer instrument (Model 12 C). In the latter case, carbon tetrachloride was used as solvent, and the following experimental data were recorded, a lithium fluoride prism and a 0·1-mm. cell being used: Methyl 3-hydroxy-2-naphthoate, 0·1 g./c.c.; absorption at 3245 cm.$^{-1}$, optical density, 0·50. Methyl salicylate, 0·12 g./c.c; absorption at 3192 cm.$^{-1}$, optical density 0·57. 2-Hydroxy-3-acetylnaphthalene, 0·04 g./c.c.; absorption in the 3100—3400 A. region (near the C–H band). 2-Hydroxy-1-acetylnaphthalene, 0·1 g./c.c.; absorption at 3360 cm.$^{-1}$, optical density 0·18. 1-Hydroxy-2-acetylnaphthalene, 0·03 g./c.c.; absorption at 3330 cm.$^{-1}$, optical density 0·07. 2-Hydroxy-1-naphthaldehyde, 0·1 g./c.c.; absorption at 3240 cm.$^{-1}$ (approx.), optical density 0·03.

Materials.—Benzoic acid, salicylic acid, methyl salicylate, *o*-methoxybenzoic acid, 3-hydroxy-2-naphthoic acid, and 2-hydroxy-1-naphthaldehyde were commercial samples; they were purified by the customary methods. Methyl *o*-methoxybenzoate was prepared by methylation of salicylic acid with an excess (3 mols.) of diazomethane; b. p. 127°/11 mm. (v. Auwers, *Annalen*, 1915, **408**, 252). Methyl 3-hydroxy-2-naphthoate was prepared according to Cohen and Dudley (*J.*, 1910, **97**, 1748; cf. Beilstein, 1st Suppl. Vol. X, p. 148); from methanol; m. p. 94°. Methyl 3-methoxy-2-naphthoate was also obtained by methylation of 3-hydroxy-2-naphthoic acid with diazomethane (3 mols.); it boiled at 217°/30 mm. and was recrystallized from light petroleum; m. p. 49° (Werner and Seybold, *Ber.*, 1904, **37**, 3661). Alkaline hydrolysis, according to Cohen and Dudley (*loc. cit.*), gave 3-methoxy-2-naphthoic acid; m. p. 133°, from dilute alcohol.

1-Acetyl-2-naphthol was prepared (Fries, *Ber.*, 1921, **54**, 711; Fries and Ehlers, *Ber.*, 1923, **56**, 1305) by Fries arrangement of 2-naphthyl acetate (Miller, *Ber.*, 1881, **14**, 1602); it boiled at 183—185°/26 mm. and crystallized from light petroleum in diamond-shaped crystals, m. p. 65°. 2-Acetyl-1-naphthol (Witt and Braun, *Ber.*, 1914, **47**, 3219) was obtained by acetylation of 1-naphthol in presence of zinc chloride as catalyst. Repeated crystallization from isopropanol and methanol gave well-defined crystals of m. p. 101°.

For the synthesis of 3-acetyl-2-naphthol the method of Fries and Schimmelschmidt was employed (*Ber.*, 1925, **58**, 2838; cf. E. Bergmann and Berlin, *loc. cit.*).

For the synthesis of the naphthoic acids, the Grignard reaction was used (*Org. Synth.*, Coll. Vol. II, p. 425; Gilman and St. John, *Rec. Trav. chim.*, 1929, **48**, 744); both acids were recrystallized from dibutyl ether; m. p. 161° and 185°, respectively.

In the determination of the ultra-violet spectra, the authors were assisted by Mrs. H. Hartstein.

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483. *The Action of Grignard Reagents on Anhydro-sugars of Ethylene Oxide Type. Part I. The Behaviour of Derivatives of α-Methyl-2 : 3-anhydroalloside towards Methylmagnesium Iodide.*

By F. H. Newth, G. N. Richards, and L. F. Wiggins.

4 : 6-Benzylidene α-methyl-2 : 3-anhydroalloside and methylmagnesium iodide give only 4 : 6-benzylidene α-methyl-3-iodo-3-deoxyglucoside, the structure of which is proved by conversion into the known 4 : 6-benzylidene 2-methyl α-methyl-3-deoxyglucoside. However, 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside gives 4 : 6-dimethyl α-methyl-2-iodo-2-deoxy-altroside, 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside, and 4 : 6-dimethyl α-methyl-3-methyl-3-deoxyglucoside. The structure of the last compound is only tentatively assigned; those of the other two are proved—that of the iodoglucose derivative by synthesis of its acetyl derivative from 4 : 6-benzylidene α-methyl-3-iodo-3-deoxyglucoside, and that of the iodoaltrose isomer by conversion into 3 : 4 : 6-trimethyl α-methyl-2-deoxy-alloside and synthesis of this material. The proportion in which the three products from 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside and methylmagnesium iodide are formed varies with the reaction temperature.

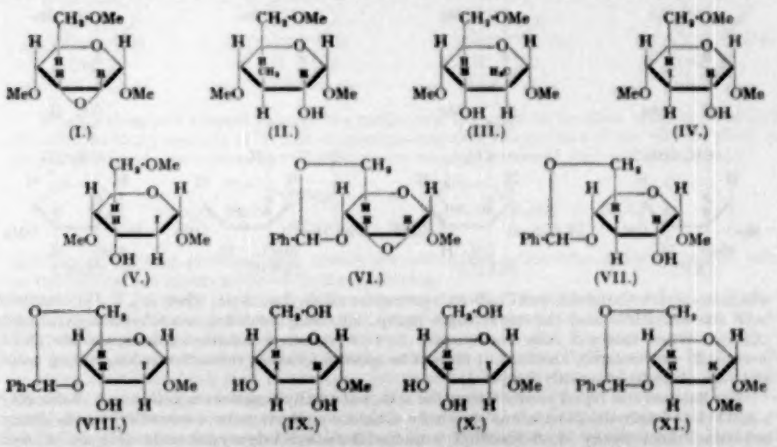
Reactions between compounds of ethylene oxide type and Grignard reagents have long been known and at first it was accepted that the normal reaction was that in which opening of the ring by RMgX occurred to yield compounds of the type R'·CHR·CH(OH)·R''. Thus, Henry (*Compt. rend.*, 1907, **145**, 453) found that propylene oxide and ethylmagnesium bromide yielded pentan-2-ol. It soon became apparent, however, that certain reactions which were at first regarded as abnormal were in fact quite common. These resolved themselves into two classes: (i) the formation of halogenohydrin derivatives, and (ii) rearrangement of the epoxy-compound to a ketone or aldehyde which then reacted with the reagent in the usual way. Blaise (*Compt. rend.*, 1902, **134**, 551) first noted that ethylene oxide and ethylmagnesium bromide formed ethylene bromohydrin, and Grignard (*Bull. Soc. chim.*, 1903, [iii], **29**, 946) then showed that,

by conducting the reaction at −15° and removing the solvent ether by distillation before hydrolysis, *n*-butyl alcohol was obtained. More recently Wiggins and Wood (*J.*, 1950, 1566) have found that the action of methylmagnesium iodide on 1 : 2-5 : 6-diepoxyhexane leads to dihydroxy-1 : 6-di-iodohexanes and that similar treatment of 3 : 4-*iso*propylidene 1 : 2-5 : 6-dianhydromannitol gives 3 : 4-*iso*propylidene 1 : 6-di-iodo-1 : 6-deoxymannitol. In fact it becomes increasingly likely that this type of reaction is the more common. The rearrangement type of reaction described for 2 : 3-epoxy-*n*-butane and 1 : 2-epoxy*iso*butane by Henry (*Compt. rend.*, 1907, **145**, 406) and for styrene oxide by Tiffeneau and Fournier (*Compt. rend.*, 1908, **146**, 697) seems at the moment to be of less importance in the field under consideration.

In view of these early results it appeared probable that the reaction between methylmagnesium iodide and an anhydro-sugar of ethylene oxide type would yield either a *C*-alkyl sugar or an iodo-sugar derivative. Moreover, if ring scission with the Grignard reagent followed the usual course (see Peat, *Adv. in Carbohydrate Chem.*, 1946, **2**, 37), two isomers of each type should be isolable. Thus, provided that ring scission of the oxide ring does in fact take place in the same way as that effected by means of acids and alkalis (Peat and Wiggins, *J.*, 1938, 1810; Newth, Overend, and Wiggins, *J.*, 1947, 18), we should expect to obtain, from 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside (I) and methylmagnesium iodide, any or all of the following compounds: 4 : 6-dimethyl α-methyl-3-methyl-3-deoxyglucoside (II), 4 : 6-dimethyl α-methyl-2-methyl-2-deoxyaltroside (III), 4 : 6-dimethy α-methyl-3-iodo-3-deoxyglucoside (IV), and 4 : 6-dimethyl α-methyl-2-iodo-2-deoxyaltroside (V). Both types of reaction will doubtless prove of value in synthetic carbohydrate chemistry.

The action of methylmagnesium iodide on two derivatives of α-methyl-2 : 3-anhydroalloside has now been investigated.

4 : 6-Benzylidene α-methyl-2 : 3-anhydroalloside (VI) and methylmagnesium iodide in boiling tetrahydropyran gave only (80%) a 4 : 6-benzylidene α-methyl-iododeoxyhexoside, characterized as the crystalline 2-toluene-*p*-sulphonate; no *C*-methyl sugar was found. That the iodo-sugar was either 4 : 6-benzylidene α-methyl-3-iodo-3-deoxyglucoside (VII) or 4 : 6-benzylidene α-methyl-2-iodo-2-deoxyaltroside (VIII) was shown by its alkaline hydrolysis to the anhydroalloside (VI) in excellent yield, this behaviour paralleling that of α-methyl-3-chloro-3-deoxyglucoside and α-methyl-2-chloro-2-deoxyaltroside (Newth, Overend, and Wiggins, *loc. cit.*). Aqueous oxalic acid removed the benzylidene group from the iodo-derivative, and a crystalline methyl-iodohexoside, which was either α-methyl-3-iodo-3-deoxyglucoside (IX) or α-methyl-2-iodo-2-deoxyaltroside (X), was obtained. Evidence in favour of (IX) was that the compound did not react with acetone and sulphuric acid; a compound (X) would have formed the 3 : 4-*iso*propylidene derivative, as does the 2-chloro-analogue (Newth, Overend, and Wiggins, *loc. cit.*). Final



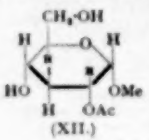
proof was obtained by methylation of the 4 : 6-benzylidene α-methyliododeoxyhexoside with silver oxide and methyl iodide to give a monomethyl derivative from which the iodine atom

was removed by hydrogenation, the product being 4 : 6-benzylidene 2-methyl α-methyl-3-deoxyglucoside (XI) (Prins, *Helv. Chim. Acta*, 1946, **29**, 1). Hence the product of the action of methylmagnesium iodide on 4 : 6-benzylidene α-methyl-2 : 3-anhydroalloside is (VII) and its acid hydrolysis product is (IX). Although the reaction of the Grignard reagent on the alloside was conducted under various conditions only the iodo-glucoside was obtained.

In view of these results, only one product, namely 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside (IV), was expected to be formed from 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside (I) and methylmagnesium iodide, but in fact a complex mixture was obtained. It was only possible to isolate the individual constituents in rather poor yields. When the reaction was conducted at 35° a crystalline and two liquid products were isolated; of the liquid substances, one contained iodine and the other did not.

The crystalline material was 4 : 6-dimethyl α-methyliodododeoxyhexoside which theoretically must be either 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside (IV) or 4 : 6-dimethyl α-methyl-2-iodo-2-deoxyaltroside (V). It afforded the original anhydroalloside (I) on alkaline hydrolysis. Its structure was finally settled as (IV) because the acetyl derivative was identical with that synthesized as follows from the known deoxyglucoside (VII). (VII) was acetylated and then hydrolysed with dilute oxalic acid, with the formation of 2-acetyl α-methyl-3-iodo-3-deoxyglucoside (XII) which on careful methylation furnished 2-acetyl 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside (XIII).

The liquid products were separated by the fractional distillation of their acetyl derivatives. Ultimate analysis showed the higher-boiling substance to be an acetyl dimethyl methyliodo-deoxyhexoside which on alkaline hydrolysis gave 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside in good yield and was clearly different from the crystalline 2-acetyl 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside, so that it is assigned the structure (XIV). The iodine atom was readily removed from this by reduction with sodium amalgam in buffered solution, which also hydrolysed the acetyl group and furnished 4 : 6-dimethyl α-methyl-2-deoxyalloside (XV). Methylation gave 3 : 4 : 6-trimethyl α-methyl-2-deoxyalloside (XVI) (sample 1). Proof of the structure of this and hence of the 4 : 6-dimethyl α-methyl-2-iodo-2-deoxyaltroside precursor was furnished by a synthetic procedure. 4 : 6-Benzylidene α-methyl-2 : 3-anhydroalloside with ethanethiol in the presence of an equivalent amount of sodium methoxide gave liquid 4 : 6-benzylidene α-methyl-2-ethylthio-2-deoxyaltroside (XVII) [Jeanloz, Prins, and Reichstein (*Helv. Chim. Acta*, 1946, **29**, 371), from methanethiol and the same anhydro-sugar, obtained the amorphous 4 : 6-benzylidene α-methyl-2-methylthio-2-deoxyaltroside and proved its structure]. Methylation of the 2-ethylthio-derivative (XVII) with methyl iodide and silver oxide gave crystalline 4 : 6-benzylidene 3-methyl α-methyl-2-ethylthio-2-deoxyaltroside (XVIII), from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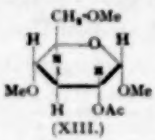
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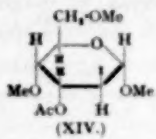
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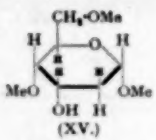
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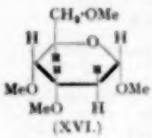
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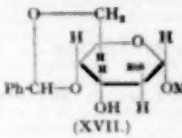
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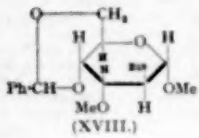
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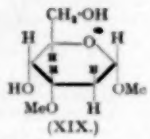
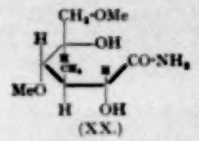

(XIX.)

which Bougault, Cattelain, and Chabrier's procedure (*Bull. Soc. chim.*, 1940, [v], **7**, 781) removed both the ethylthio- and the benzylidene group, affording 3-methyl α-methyl-2-deoxyalloside (XIX). When this was fully methylated, 3 : 4 : 6-trimethyl α-methyl-2-deoxyalloside (XVI) (sample 2) was isolated, identical in respect to specific rotation, refractive index, boiling point, and rate of hydrolysis with sample 1.

The halogen-free liquid product from the action of methylmagnesium iodide on 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside was shown by ultimate analysis to be a trimethyl methyldeoxyhexoside—theoretically 4 : 6-dimethyl α-methyl-3-methyl-3-deoxyglucoside (II) or 4 : 6-dimethyl α-methyl-2-methyl-2-deoxyaltroside (III). Its identity has not yet been definitely established but evidence is presented that it at least contains the glucoside (II). The main

difficulty has been failure to obtain crystalline derivatives (it formed a liquid toluene-*p*-sulphonate derivative, and after acidic hydrolysis gave a non-crystalline trimethyl deoxyhexose). Oxidation of the free sugar with bromine water gave a carboxylic acid lactone, but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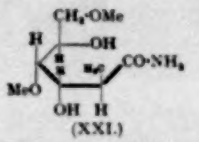
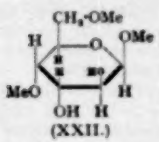

(XXI.)

neither this nor its amide was solid. Whether this amide is (XX) or (XXI) depends on whether the glycoside precursor is a derivative of glucose (II) or altrose (III). The amide (XX), possessing a hydroxyl group adjacent to the carbamyl group, should give a positive Weerman test; the altronamide (XXI) is not an α-hydroxy-amide. The syrupy amide isolated did in fact respond to the Weerman reaction and hence must at least contain the gluconamide (XX).

When methylmagnesium iodide and 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside reacted in ether at 35°, only 5·8% of the crystalline product, 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside, was obtained, but at −15° the yield of this was 36·8%. At 86° in boiling tetrahydropyran, a still higher yield of 42% was obtained. The low yield of iodo-glucoside at 35° was not fortuitous since similar results were obtained when the experiment was repeatedly carried out.

Discussion.—Scission of an ethylene oxide ring asymmetrically situated in a sugar molecule has been shown to take place in both possible directions, invariably with Walden inversion, whether the reagent is alkaline or acidic. Thus, 4 : 6-dimethyl β-methyl-2 : 3-anhydroalloside and hot sodium hydroxide solution gave both 4 : 6-dimethyl β-methylaltroside (XXII) and 4 : 6-dimethyl β-methylglucoside (XXIII) (Peat and Wiggins, *J.*, 1938, 1810). Similarly treatment of 4 : 6-benzylidene α-methyl-2 : 3-anhydroalloside with hydrochloric acid in aqueous acetone effected hydrolysis of the benzylidene residue and scission of the anhydro-ring with the formation of α-methyl-3-chloro-3-deoxyglucoside (XXIV) and α-methyl-2-chloro-2-deoxyaltroside (XXV) (Newth, Overend, and Wiggins, *loc. cit.*).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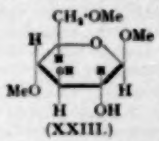
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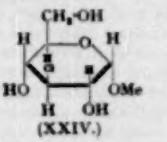
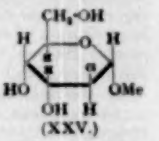

(XXIV.)


(XXV.)

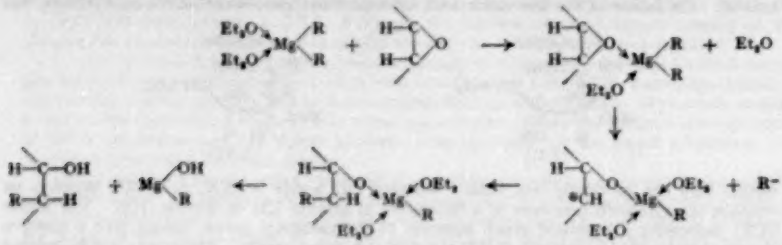
When a Grignard reagent attacks the oxide ring the mode of reaction must be essentially the same as that occurring with acid or alkaline reagents, irrespective of the way in which the Grignard reagent itself behaves. The Grignard reagent, however, may ionise two ways:

$$2RMgX \rightleftharpoons \begin{bmatrix} RMg^+ & + & X^- \\ R^- & + & MgX^+ \end{bmatrix} \rightleftharpoons R_2Mg + MgX_2$$

and any of the ions produced may attack the carbonium cation transiently formed at either of the two carbon atoms involved in the oxide ring.

There will assuredly be a competition between the two reagents R^- and X^-. Attack on the carbonium cation by R^- will lead to *C*-alkyl-sugar derivatives, whereas that by X^- will result in the formation of halogeno-derivatives. The ions R^- and X^- may arise, however, on the decomposition of a complex of the ethylene oxide ring with MgR_2 or with MgX_2. This complex may arise from that of the type proposed by Meisenheimer and Casper (*Ber.*, 1921, **54**, 1655) for a Grignard reagent and ether, by the substitution of one of the ether molecules with the ethylene oxide compound; it may be formed by the anhydro-sugar and either the dialkylmagnesium or the magnesium dihalide. Its hydrolysis would be expected to lead to the formation of R^- or X^- together with a carbonium cation liable to attack (accompanied by Walden inversion) by these ions. The following scheme represents a possible course for the

reaction of the ethylene oxide with dialkylmagnesium and may equally be applied to that involving magnesium dihalides:



Since experiments have demonstrated that the reaction of a Grignard reagent with 4 : 6-dimethyl and 4 : 6-benzylidene α-methyl-2 : 3-anhydroalloside leads primarily to the iodo-sugar derivatives the main attack on the oxide ring is by the iodide ion, probably produced from the decomposition of an intermediate complex. This being the case, it would be expected that magnesium iodide itself could effect ring scission of the ethylene oxide ring. When this reagent was heated in ethereal solution with either 4 : 6-benzylidene or 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside, 4 : 6-benzylidene and 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside respectively were obtained. The action of other magnesium halides on anhydro-sugars of ethylene oxide type is being studied and it appears that this reaction provides a convenient and apparently a general method of preparing halogeno-sugars. Also, since in certain cases these halogen atoms may be replaced by hydrogen, the procedure leads to the synthesis of deoxy-sugars. The formation of halohydrins from non-sugar ethylene oxides and magnesium halides has been observed by Ribas and Tapia (*Anal. Fís. Quím.*, 1930, **28**, 636) who isolated 1-bromo-1-chloropropan-2-ol after treating epichlorohydrin with magnesium bromide in ether and obtained 1 : 3-dichloropropan-2-ol when epichlorohydrin was treated with zinc chloride in ether.

The formation of the more interesting *C*-alkyl sugars will doubtless involve the reaction of dialkylmagnesium or other similar organometallic derivative with the ethylene oxide compound. It has already been mentioned that these substances may be formed through the isomerisation of the ethylene oxide to a ketone and the subsequent action of the Grignard reagent thereon. The mode of formation of the *C*-alkyl sugars is however at present under investigation and we prefer to make no definite statement about the mechanism now.

In the reaction of the benzylidene anhydroalloside (VI) with methylmagnesium iodide, only 4 : 6-benzylidene α-methyl-3-iodo-3-deoxyglucoside (VII) was obtained and that in 80% yield. It is noteworthy that when the same anhydro-compound was treated with sodium methoxide or ammonia (*J.*, 1938, 1810) the main product, obtained in approximately 90% yield, was respectively a 2-methyl- or 2-amino-altrose derivative, the 3-methyl- or 3-amino-glucose derivative being obtained in, at most, 10% yield. Thus, in this particular case the relative proportions of ring scission products were reversed when the reagent used was magnesium iodide. The altrose isomer was also a minor constituent amongst the products of the more complex reaction of methylmagnesium iodide with 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside.

Experimental.

Treatment of 4 : 6-*Benzylidene* α-*Methyl*-2 : 3-*anhydroalloside with Methylmagnesium Iodide.*—The alloside (7·0 g.) (Richtmyer and Hudson, *J. Amer. Chem. Soc.*, 1941, **63**, 1727), m. p. 199—200°, dissolved in warm dry tetrahydropyran (200 c.c.), was added to a Grignard reagent prepared by warming methyl iodide (5·0 g.) in dry tetrahydropyran with magnesium turnings (0·9 g.) for 2 hours. An exothermic reaction took place and a white solid separated. The mixture was boiled for 2 hours, cooled, and treated with powdered ice, followed by dilute hydrochloric acid until all the solid had dissolved. The tetrahydropyran layer was separated and the aqueous layer extracted with a further quantity of solvent. The combined extracts were washed with dilute sodium carbonate solution and with water, dried ($MgSO_4$), filtered, and evaporated. Crystalline 4 : 6-*benzylidene* α-*methyl*-3-*iodo*-3-*deoxyglucoside* (12·6 g., 80%) remained. This, after being recrystallised from alcohol, had m. p. 195—196° and $[\alpha]_D^{18}$ −8·0° (*c*, 1·00 in chloroform) (Found: C, 42·8; H, 4·3; OMe, 8·3. $C_{14}H_{17}O_5I$ requires C, 42·9; H, 4·4; OMe, 7·9%). No other product was isolated.

4 : 6-*Benzylidene* 2-*Toluene*-p-*sulphonyl* α-*Methyl*-3-*iodo*-3-*deoxyglucoside.*—The above compound (0·2 g.) was treated in dry pyridine with toluene-*p*-sulphonyl chloride (0·15 g.) at room temperature.

After being kept overnight the solution was poured into water and the white precipitate was collected, washed with water, and recrystallised from alcohol. The *2-toluene-p-sulphonate* formed colourless crystals (0·19 g.), m. p. 137·5—138·5°, $[\alpha]_D^{20}$ −4·3° (*c*, 0·537, in chloroform) (Found: C, 46·5; H, 4·3. $C_{21}H_{22}O_7IS$ requires C, 46·1; H, 4·2%).

Treatment of 4 : 6-*Benzylidene* α-*Methyl*-3-*iodo*-3-*deoxyglucoside with Sodium Methoxide.*—The glucoside (0·156 g.) was dissolved in chloroform (1·5 c.c.) and a solution of sodium (0·12 g.) in dry methanol (6 c.c.) added at 0°. After 1 hour at room temperature needle-shaped crystals began to separate. On the next day these (0·102 g.) were collected, recrystallised from alcohol, and had m. p. 199—200° alone or on admixture with an authentic specimen of 4 : 6-benzylidene α-methyl-2 : 3-anhydroalloside.

Hydrolysis of 4 : 6-*Benzylidene* α-*Methyl*-3-*iodo*-3-*deoxyglucoside with Oxalic Acid.*—The glucoside (5·0 g.) was dissolved in acetone (225 c.c.), and a solution of oxalic acid (7·5 g. of the hydrate in 25 c.c. of water) was added. The solution was boiled for 100 hours, the specific rotation becoming constant after 85 hours. The acid was neutralised with barium carbonate, the solids were removed by filtration, and the solution was evaporated to dryness under reduced pressure. The residue of α-*methyl*-3-*iodo*-3-*deoxyglucoside* (2·9 g.), recrystallised from ethyl acetate, had m.p. 165° and $[\alpha]_D^{20}$ +136° (*c*, 1·00 in dioxan) (Found: C, 27·7; H, 4·3; OMe, 10·2. $C_7H_{13}O_5I$ requires C, 27·6; H, 4·3; OMe, 10·2%).

Attempted Condensation of α-*Methyl*-3-*iodo*-3-*deoxyglucoside with Acetone.*—The compound (0·201 g.) and concentrated sulphuric acid (0·13 c.c.) in dry acetone (15 c.c.) were kept overnight. Thereafter, the mixture was neutralised with anhydrous sodium carbonate, filtered, and evaporated. The residue, recrystallised from ethyl acetate, had m.p. 165° alone or on admixture with the original material.

Methylation of 4 : 6-*Benzylidene* α-*Methyl*-3-*iodo*-3-*deoxyglucoside.*—The glucoside (0·634 g.) was treated thrice with silver oxide and methyl iodide in the usual way, the product being extracted with chloroform. After the third methylation treatment, evaporation of the chloroform extract furnished 4 : 6-*benzylidene* 2-*methyl* α-*methyl*-3-*iodo*-3-*deoxyglucoside* as feathery needles which, recrystallised from chloroform–ether, had m. p. 193°, $[\alpha]_D^{20}$ −23·2° (*c*, 0·5 in chloroform) (Found: C, 44·0; H, 4·9. $C_{14}H_{19}O_5I$ requires C, 44·3; H, 4·7%).

Hydrogenation of 4 : 6-*Benzylidene* 2-*Methyl* α-*Methyl*-3-*iodo*-3-*deoxyglucoside.*—The above methylated glucoside (0·324 g.) was dissolved in a mixture of ether (30 c.c.) and methanol (30 c.c.). Potassium hydroxide (1 g.) and 10% palladised charcoal (0·2 g.) were added and the mixture hydrogenated at slightly elevated pressure, there being a steady absorption of hydrogen during 1 hour. Thereafter the solution was filtered, the charcoal was washed with ether, and the combined filtrates were evaporated to dryness. The residue was extracted with chloroform, and the extract filtered and then evaporated. The residual syrup completely crystallised and, recrystallised from aqueous ethanol, had m.p. 78° alone or on admixture with the 4 : 6-benzylidene 2-methyl α-methyl-3-deoxyglucoside of Newth, Overend, and Wiggins (*loc. cit.*).

Reaction of 4 : 6-*Dimethyl* α-*Methyl*-2 : 3-*anhydroalloside and Methylmagnesium Iodide.*—(a) *At* 35°. To a solution of methyl iodide (12·7 g.) in ether (50 c.c.) were added magnesium turnings (2·14 g.) and the mixture was warmed until reaction commenced. Thereafter the mixture was heated under reflux until all the metal had dissolved. The solution was then cooled and an ethereal solution of 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside (14·5 g.) added to a cooled solution from methyl iodide (12·7 g.) and magnesium (2·14 g.) in dry ether (50 c.c.). An immediate exothermic reaction occurred, accompanied by precipitation of a white solid. The mixture was heated under reflux for 2 hours, cooled, and treated with powdered ice, followed by dilute hydrochloric acid. The ethereal layer was separated, the aqueous portion extracted with more ether, and the extracts combined; after being washed with sodium hydrogen carbonate solution and water, the extract was dried ($MgSO_4$) and concentrated. Crystals of 4 : 6-*dimethyl* α-*methyl*-3-*iodo*-3-*deoxyglucoside* (0·82 g.) separated. These were collected and the mother-liquors kept. The aqueous layer was exactly neutralised with 5*N*-sodium hydroxide and evaporated to dryness. The residue was extracted several times with boiling chloroform, and the extracts were combined with the above ethereal mother-liquors and evaporated. The yellow syrup obtained was kept for several days, whereupon a further quantity of 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside separated. This, recrystallised from ether, had m. p. 112·5—113° and $[\alpha]_D^{20}$ +119·9° (*c*, 1·031 in chloroform) (Found: C, 32·9; H, 5·2; I, 39·0. $C_9H_{17}O_5I$ requires C, 32·5; H, 5·2; I, 38·25%). The total yield of the 3-iodo-compound was 1·38 g. (5·8%). A mixture of the residual brown syrup (12·5 g.) and acetic anhydride (25 c.c.) in dry pyridine (60 c.c.) was kept overnight at room temperature and then poured into water, and the solution extracted with chloroform. The extract was washed with water, dried ($CaCl_2$), filtered, and evaporated. The syrup obtained (13·5 g.) was then fractionally distilled, giving pure (?) 2-*acetyl* 4 : 6-*dimethyl* α-*methyl*-3-*methyl*-3-*deoxyglucoside*, b. p. 110° (bath-temp.)/0·02 mm., n_D^{20} 1·4593, $[\alpha]_D^{20}$ +108·5° (*c*, 1·087 in chloroform) (2·45 g., 15·9%) (Found: C, 54·6; H, 8·2; OMe, 35·0. $C_{12}H_{22}O_5$ requires C, 54·9; H, 8·5; OMe, 35·5%). All the material which distilled above 110°/0·02 mm. contained iodine and appeared to be a mixture of isomeric dimethyl methyliodohexosides. It was passed in light petroleum (b.p. 60—80°) through a column of alumina. Elution with light petroleum (b.p. 60—80°) gave a first fraction which was again purified by passage through alumina, whereupon 3-*acetyl* 4 : 6-*dimethyl* α-*methyl*-2-*iodo*-2-*deoxyaltroside* was obtained as a pale yellow syrup. After being dried at 60°/0·2 mm. for 2 hours it showed n_D^{20} 1·4948, $[\alpha]_D^{20}$ +70·0° (*c*, 0·957 in chloroform) (Found: C, 36·0; H, 5·4. $C_{11}H_{19}O_5I$ requires C, 35·3; H, 5·1%) (total yield, 1·8 g., 6·8%).

(b) *At* −15°. The Grignard reagent from methyl iodide (1·5 g.), magnesium (0·255 g.), and ether (10 c.c.) was cooled to −15° (ice–salt) and a saturated solution of 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside (2 g.) in ether (50 c.c.), also at −15°, was slowly added with stirring. A white solid separated. The mixture was allowed to attain room temperature while stirring was continued overnight. Thereafter, the ether was removed by distillation at atmospheric pressure. Ice was added to the residue,

followed by chloroform (10 c.c.) and dilute hydrochloric acid sufficient to dissolve the magnesium hydroxide. The chloroform layer was separated and the aqueous portion extracted several times with chloroform. The extracts were combined, washed with dilute sodium hydrogen carbonate solution and with water, dried ($CaCl_2$), and evaporated. The syrup obtained crystallised on trituration with ether and, recrystallised from ether, gave colourless needles of 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside (1·2 g., 37%), m. p. 111—112° alone or on admixture with authentic material. The mother-liquors yielded no other crystalline material except unchanged anhydroalloside (0·1 g.).

(c) *At 86°.* To a boiling Grignard reagent prepared from methyl iodide (0·76 g.) and magnesium (0·13 g.) in tetrahydropyran (10 c.c.), a solution of 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside was added dropwise. After 1 hour's heating a fine white granular precipitate separated. The solution was then cooled and ice added, followed by hydrochloric acid. The tetrahydropyran layer was separated and washed with dilute sodium hydrogen carbonate and sodium thiosulphate solutions and with water. After being dried ($MgSO_4$) the solution was evaporated to dryness. The partly crystalline residue, recrystallised from ether, afforded 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside (0·546 g., 33·1%), m.p. 111·5—112·5° alone or on admixture with an authentic specimen. The aqueous layer from the reaction mixture was extracted exhaustively with chloroform. The extracts were washed as before and combined with the ethereal mother-liquors, and the mixture was evaporated to dryness. The residue was a liquid which distilled in two fractions: (i) b. p. 103—110° (bath-temp.)/0·05 mm. (45 mg.), n_D^{25} 1·4653, $[\alpha]_D^{25}$ +74·0° (*c*, 0·423 in chloroform), and (ii) b. p. 130—135° (bath-temp.)/0·045 mm. (0·30 g.). The syrup (ii) partly crystallised and when recrystallised afforded 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside (0·15 g., 9·2%). The residual syrup (0·10 g.), n_D^{25} 1·5005, $[\alpha]_D^{25}$ +96·2° (*c*, 1·68 in chloroform), was not investigated further. Fraction (i) probably contained 4 : 6-dimethyl α-methyl-3-methyl-3-deoxyglucoside.

Reaction between Magnesium Iodide and 4 : 6-*Dimethyl* α-*Methyl*-2 : 3-*anhydroalloside*.—A solution of the alloside (0·491 g.) in absolute ether (20 c.c.) was added slowly to a well stirred suspension of anhydrous magnesium iodide (1·3 g., 2 mols.) in the same solvent (20 c.c.) at room temperature. No change in the appearance of the mixture occurred and no appreciable heat was evolved. The mixture was heated under reflux and stirring continued for 2½ hours. After the mixture had cooled, water (20 c.c.) was added; the aqueous layer was now alkaline and a small excess of hydrochloric acid was added. The ethereal layer was separated, washed with sodium hydrogen carbonate and thiosulphate solutions, then with water, and finally dried (Na_2SO_4). On evaporation, a white solid residue (0·240 g., 30·0%) was obtained which, recrystallised from light petroleum (b.p. 60—80°), had m. p. 112—113° alone or on admixture with authentic 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside.

The aqueous layer from the reaction mixture was neutralised with sodium hydrogen carbonate and evaporated to dryness. The dry residue was extracted with boiling chloroform and the extracts evaporated to a yellow syrup (0·290 g.) which partly crystallised. The crystalline material was separated by filtration through sintered glass and was 4 : 6-dimethyl α-methyl-3-iodo-3-deoxyglucoside (0·124 g., 15·5%), m. p. 112—113°. The remaining yellow syrup (0·15 g., 18·8%) contained iodine and showed n_D^{25} 1·5168; it probably contained 4 : 6-dimethyl α-methyl-2-iodo-2-deoxyaltroside.

Acetylation of 4 : 6-*Dimethyl* α-*Methyl*-3-*iodo*-3-*deoxyglucoside*.—The glucoside (1·58 g.), treated in dry pyridine (10 c.c.) at 0° with acetic anhydride (2 c.c.), was kept at room temperature overnight and then poured into ice–water. The mixture was extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), filtered, and evaporated. The syrupy 2-*acetyl* derivative (sample 1) (1·69 g.), crystallised and recrystallised from light petroleum, had m. p. 66·5—67° and $[\alpha]_D^{25}$ +115° (*c*, 1·021 in chloroform) (Found: C, 35·7; H, 4·9. $C_{11}H_{19}O_6I$ requires C, 35·3; H, 5·1%).

2-*Acetyl* 4 : 6-*Benzylidene* α-*Methyl*-3-*iodo*-3-*deoxyglucoside*.—4 : 6-Benzylidene α-methyl-3-iodo-3-deoxyglucoside (1·25 g.) was treated in dry pyridine (10 c.c.) at 0° with acetic anhydride (2 c.c.). After being kept overnight at room temperature the mixture was poured on ice. The *acetyl* derivative which separated was collected and recrystallised from alcohol, forming prisms, m. p. 163—164°, $[\alpha]_D^{25}$ −16·4° (*c*, 1·016 in chloroform) (Found: C, 44·5; H, 4·4. $C_{18}H_{23}O_6I$ requires C, 44·2; H, 4·4%).

2-*Acetyl* α-*Methyl*-3-*iodo*-3-*deoxyglucoside*.—The foregoing acetyl derivative (1·16 g.) in acetone (40 c.c.), mixed with oxalic acid hydrate (1·7 g.) in water (7 c.c.), was boiled under reflux, and the reaction followed polarimetrically, the following data being obtained: $[\alpha]_D$ −9·7° (5 mins.), −2·4° (1 hr.), +47° (10 hrs.), +90° (30 hrs.). Thereafter the solution was cooled and neutralised with barium carbonate, the solids were filtered off, and the acetone was removed from the filtrate by evaporation. A small amount of unchanged starting material separated at this stage. Benzaldehyde present in the solution was removed by extraction with ether, the aqueous phase being evaporated to dryness. The residue crystallised and after extraction with alcohol and recrystallisation from alcohol–ether yielded 2-*acetyl* α-*methyl*-3-*iodo*-3-*deoxyglucoside* (0·79 g.), m. p. 132—132·5°, $[\alpha]_D^{25}$ +146·0° (*c*, 0·513 in ethyl alcohol). The substance softened at 127° and did not finally melt until 150°, but, after cooling, remelted sharply at 132—132·5° (Found: C, 30·8; H, 4·4; OMe, 8·9. $C_9H_{15}O_6I$ requires C, 31·2; H, 4·4; OMe, 9·0%).

2-*Acetyl* 4 : 6-*Dimethyl* α-*Methyl*-3-*iodo*-3-*deoxyglucoside* (Sample 2).—The above compound (0·7 g.) was methylated by three successive treatments with silver oxide and methyl iodide, the product of each treatment being extracted with boiling chloroform. The final product was distilled in two fractions: (i) b.p. 115—120° (bath-temp.)/0·007 mm. (0·25 g.), which was a mixture and appeared to contain anhydro-sugar derivatives; and (ii) b. p. 115° (bath-temp.)/0·007 mm. (0·10 g.). Fraction (ii) crystallised spontaneously and, recrystallised from light petroleum, had m. p. 66·5—67° alone or on admixture with sample 1 of the 2-acetyl derivative described above.

Alkaline Hydrolysis of 4 : 6-*Dimethyl* α-*Methyl*-3-*iodo*-3-*deoxyglucoside*.—The glucoside (0·126 g.), dissolved in methyl alcohol (5 c.c.), was treated with a solution of sodium (0·1 g.) in methyl alcohol

(5 c.c.). After being kept overnight at room temperature the solution was neutralised with solid carbon dioxide, water was added, and the solution extracted with chloroform. The extract was dried ($CaCl_2$) and evaporated to a syrup which rapidly crystallised. Recrystallised from light petroleum it formed 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside, long needles, m. p. 60—62° alone or on admixture with an authentic specimen.

Alkaline Hydrolysis of 3-*Acetyl* 4 : 6-*Dimethyl* α-*Methyl*-2-*iodo*-2-*deoxyaltroside*.—To the altroside (0·125 g.) in chloroform (2 c.c.), a solution of sodium (0·1 g.) in methyl alcohol (5 c.c.) was added at 0°. The solution was kept overnight but no change in optical rotation was observed; after it had been kept for 8 days at room temperature sodium iodide had separated. The solution was then neutralised with solid carbon dioxide and the mixture treated as described above. The syrup eventually obtained (50 mg.) crystallised and, after being recrystallised from light petroleum, the 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside showed m.p. 60—61° alone or on admixture with an authentic specimen.

Reduction of 3-*Acetyl* 4 : 6-*Dimethyl* α-*Methyl*-2-*iodo*-2-*deoxyaltroside*.—The altroside (1·27 g.) was dissolved in methyl alcohol (100 c.c.) and water (25 c.c.), a few drops of phenolphthalein were added, and the solution was saturated with carbon dioxide. Sodium amalgam (80 g.; 3%) was added while carbon dioxide was passed through the solution and the mixture stirred. When the amalgam had all decomposed the solution was decanted and evaporated to dryness, hydrochloric acid being added from time to time to remove alkalinity. The dry residue was extracted with ethyl acetate and the extract evaporated to a syrup (0·312 g.). In order to ensure that no acetyl groups remained in the product it was treated with sodium (0·05 g.) in dry methyl alcohol (50 c.c.). After being kept overnight, the solution showed $[\alpha]_D^{20}$ +175° and was evaporated to a pale yellow syrup (0·28 g., 40%). This was purified by chromatography on alumina from benzene solution. The product, 4 : 6-*dimethyl* α-*methyl*-2-*deoxyalloside*, was a syrup (0·17 g.) which, after being dried at 40°/0·5 mm. for 1 hr., showed n_D^{20} 1·4602 and $[\alpha]_D^{20}$ +180° (*c*, 0·194 in chloroform) (Found: C, 53·0; H, 8·7. $C_9H_{18}O_5$ requires C, 52·4; H, 8·8%).

3 : 4 : 6-*Trimethyl* α-*Methyl*-2-*deoxyalloside*.—The foregoing deoxyalloside (150 mg.) was methylated by three successive treatments with methyl iodide and silver oxide under the usual conditions. The *trimethyl* derivative (sample 1) (155 mg.) distilled at 110° (bath-temp.)/0·7 mm. and showed n_D^{20} 1·4505 and $[\alpha]_D^{20}$ +164° (*c*, 1·131 in chloroform) (Found: C, 54·2; H, 8·7. $C_{12}H_{24}O_5$ requires C, 54·5; H, 9·2%).

Synthesis of 3 : 4 : 6-*Trimethyl* α-*Methyl*-2-*deoxyalloside*. *The Reaction between Ethanethiol and* 4 : 6-*Dimethyl* α-*Methyl*-2 : 3-*anhydroalloside*.—The alloside (2 g.) was added to a solution of sodium (0·7 g.) and ethanethiol (2 g.) in dry methyl alcohol (20 c.c.), and the mixture boiled for 2 hours. Complete dissolution was effected within 10 minutes. After being cooled, the solution was evaporated to half its bulk. Water (3 c.c.) was then added and the rest of the methyl alcohol removed. The resulting oily suspension was extracted several times with ether (total, 50 c.c.), and the extract washed with water and dried (Na_2SO_4). Evaporation yielded a colourless syrup (2·245 g., 91%). Part of the product (0·95 g.) was purified by chromatography on an alumina column (8″ × ¾″) from benzene solution, the product being eluted with the same solvent. 4 : 6-*Benzylidene* α-*methyl*-3-*ethylthio*-2-*deoxyaltroside* recovered from the early fractions (0·648 g.) showed n_D^{20} 1·5485 and $[\alpha]_D^{20}$ +79·2° (*c*, 1·022 in chloroform) after being dried at 60°/0·04 mm. for 1 hour (Found: C, 59·0; H, 6·7. $C_{15}H_{20}O_4S$ requires C, 58·9; H, 6·6%). The material was distilled with slight decomposition but the distillate had the characteristics shown above. The *acetate*, prepared by treating the syrup (0·27 g.) in dry pyridine (2 c.c.) with acetic anhydride (0·5 c.c.) at 0° for 24 hours, separated as an oil when the mixture was poured into ice-water. It was extracted with chloroform, the extracts being washed with water and dried ($MgSO_4$), and obtained as a syrup, b.p. 190—200° (bath-temp.)/0·4 mm., n_D^{20} 1·5337, $[\alpha]_D^{20}$ +83·6 (*c*, 1·315 in chloroform) (Found: C, 58·2; H, 6·7. $C_{17}H_{22}O_5S$ requires C, 58·7; H, 6·6%).

4 : 6-*Benzylidene* 3-*Methyl* α-*Methyl*-2-*ethylthio*-2-*deoxyaltroside*.—The 2-ethylthio-derivative obtained as above (0·249 g.) was methylated by three successive treatments with methyl iodide and silver oxide in the usual way, the product being extracted with chloroform. The final extracts were evaporated to a yellow liquid which, after distillation at 190—200° (bath-temp.)/0·1 mm., crystallised spontaneously and recrystallised from ether. 4 : 6-*Benzylidene* 3-*methyl* α-*methyl*-2-*ethylthio*-2-*deoxyaltroside* formed fine white needles, m. p. 96—97° (0·23 g., 88%), $[\alpha]_D^{20}$ +74·7° (*c*, 1·112 in chloroform) (Found: C, 59·5; H, 7·1. $C_{17}H_{24}O_4S$ requires C, 59·9; H, 7·1%).

Reduction of 4 : 6-*Benzylidene* 3-*Methyl* α-*Methyl*-2-*ethylthio*-2-*deoxyaltroside with Alkaline Raney Nickel*.—The altroside (1·31 g.) was dissolved in ethyl alcohol (60 c.c.), Raney nickel (*ca.* 25 g.; freshly prepared and washed with water until the washings showed pH 10, then with alcohol until the washings showed pH 9) was added, followed by water (20 c.c.), and the mixture was heated under reflux for 2 hours. The nickel was then filtered off and washed with water. The odour of toluene was detectable in the filtrate. This was evaporated to dryness under reduced pressure and the syrupy residue dissolved in water (10 c.c.) and shaken with chloroform to remove unchanged starting material. The aqueous layer was saturated with hydrogen sulphide in the presence of ammonia and filtered. The filtrate was evaporated to dryness and the residue dried thoroughly by evaporation with benzene. The residue was extracted with chloroform to remove still further amounts of inorganic material. The final product obtained on evaporation of the chloroform was a colourless syrup (0·68 g., 91%) which distilled at 105—110° (bath-temp.)/0·3 mm. as an oil, n_D^{20} 1·4772, $[\alpha]_D^{20}$ +201° (*c*, 0·609 in chloroform) (Found: C, 49·8; H, 8·6. Calc. for $C_9H_{16}O_5$: C, 50·0; H, 8·4%). It was 3-methyl α-methyl-2-deoxyalloside. Reichstein *et al.* (*loc. cit.*) give $[\alpha]_D^{20}$ +196·5° for this substance.

Methylation of 3-*Methyl* α-*Methyl*-2-*deoxyalloside*.—The above alloside (0·587 g.) was methylated by three successive treatments with methyl iodide and silver oxide at 45° for 12 hours in the usual way, the product being extracted after each treatment with boiling chloroform. Evaporation of the final extract gave a liquid 3 : 4 : 6-trimethyl ether (0·559 g.) which distilled at 70—75° (bath-temp.)/0·2 mm.,

as a colourless mobile oil (0·43 g.), n_D^{25} 1·4510, $[\alpha]_D^{25}$ +183·0° (*c*, 1·298 in chloroform) (Found : C, 54·2; H, 9·0. Calc. for $C_{10}H_{20}O_5$: C, 54·5; H, 9·2%). It was identical with sample 1 recorded above.

Hydrolysis of 3 : 4 : 6-*Trimethyl* α-*Methyl*-2-*deoxyalloside* (*Samples* 1 *and* 2).—The trimethyl alloside (sample 2) (0·176 g.) was dissolved in ethyl alcohol (7·5 c.c.) at room temperature and 16% hydrochloric acid (0·5 c.c.) added. The mixture was kept at room temperature and the hydrolysis followed polarimetrically : $[\alpha]_D^{25}$ +190° (3 mins.); +150° (32 mins.); +122·6° (112 mins.); + 81·0° (4 hrs.); +63·5° (6 hrs.); +51° (24 hrs., constant). Similarly sample 1 (0·043 g.) in alcohol (3·75 c.c.) was treated with 16% hydrochloric acid (0·25 c.c.) at room temperature. The changes in specific rotation were : $[\alpha]_D^{25}$ +198° (4 mins.); +157·4° (57 mins.); +120·4° (2½ hrs.); +86·2° (4 hrs.); +66·6° (6½ hrs.); +51·6° (25 hrs., constant).

4 : 6-*Dimethyl* α-*Methyl*-3-*methyl*-3-*deoxyglucoside*.—2-Acetyl 4 : 6-dimethyl α-methyl-3-methyl-3-deoxyglucoside (2·23 g.), obtained by the action of methylmagnesium iodide on 4 : 6-dimethyl α-methyl-2 : 3-anhydroalloside at 35°, was deacetylated by dissolving it in dry methyl alcohol, adding a small piece of sodium, and keeping the solution at room temperature. The following changes in specific rotation were observed : $[\alpha]_D$ +63·5° (20 mins.); +57·6° (4 hrs.); +54·0° (24 hrs.). Thereafter, the solution was evaporated to a syrup which distilled at 80° (bath-temp.)/0·02 mm. The colourless distillate (1·25 g., 67%), n_D^{25} 1·4640, $[\alpha]_D^{25}$ +73·5° (*c*, 1·305, in chloroform), was probably 4 : 6-dimethyl α-methyl-3-methyl-3-deoxyglucoside (Found : C, 54·8; H, 9·7. Calc. for $C_{10}H_{20}O_5$: C, 54·5; H, 9·2%). Treatment with toluene-*p*-sulphonyl chloride in pyridine gave a syrup, $[\alpha]_D^{25}$ +47·9° (*c*, 1·92, in chloroform) (Found : C, 54·7; H, 6·7. Calc. for $C_{17}H_{26}O_7S$: C, 54·5; H, 7·0%).

Hydrolysis of 4 : 6-*Dimethyl* α-*Methyl*-3-*methyl*-3-*deoxyglucoside*.—The glucoside (1·40 g.) was heated at 100° with 5% hydrochloric acid (25 c.c.) and the reaction followed polarimetrically : $[\alpha]_D$ +35·5° (initial); −29·6° (5 mins.); −29·4° (10 mins., constant). Thereafter the solution was neutralised with barium carbonate, filtered, and evaporated. The dry residue was extracted several times with boiling chloroform, and the extracts were evaporated to a viscous syrup (1·147 g.), which distilled (with some difficulty) at 130° (bath-temp.)/0·06 mm. and showed n_D^{25} 1·4540 and $[\alpha]_D^{25}$ −24·4° (*c*, 0·858 in water). It was probably 4 : 6-dimethyl 3-methyl-3-deoxyglucose (Found : C, 51·6; H, 8·0. Calc. for $C_9H_{18}O_5$: C, 52·4; H, 8·8%).

Formation of Hydrazodicarboxyamide from 4 : 6-*Dimethyl*-3-*methyl*-3-*deoxyglucose*.—The glucose derivative (0·223 g.) was dissolved in water (10 c.c.), bromine (0·5 c.c.) added, and the mixture kept in a stoppered flask at 35° for 20 hours. Excess of bromine was then removed by aeration and the solution neutralised with silver carbonate. The solids were filtered off and washed with water, and the filtrate was saturated with hydrogen sulphide. After the precipitated silver sulphide had been removed by filtration, the clear liquid was evaporated to a yellow syrup (0·104 g.). This was heated at 50°/0·2 mm. for a hour over phosphoric oxide to effect lactonisation and then dissolved in dry methyl alcohol (5 c.c.), and the solution was saturated with ammonia at 0°. After being kept at 15° for 40 hours under pressure the mixture was filtered and evaporated in a vacuum. A yellow amorphous solid (0·073 g.) was obtained which could not be crystallised. This was dissolved in water (1 c.c.), cooled to 0°, and treated with 1·5*N*-sodium hypochlorite (0·5 c.c.) for 30 minutes. Excess of hypochlorite was removed by the careful addition of sodium thiosulphate (starch–iodide), and solid sodium acetate (0·5 g.) was added. The solution was then filtered and treated with semicarbazide hydrochloride (0·075 g.). Hydrazodicarboxyamide separated rapidly as a fine white crystalline precipitate which was removed by centrifuging and washed with water; it (5 mg.) had m. p. 252° (decomp.), not depressed on admixture with an authentic specimen (m. p. 258°).

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484. *Heteropoly-tungstic Acids and Heteropoly-tungstates. Part I.* 11-*Tungstoferric*(III) *Acid and its Salts.*

By JOHN A. MAIR.

The reaction between ferric salts and sodium paratungstate in boiling aqueous solution has been investigated, and 11-tungstoferric(III) acid, the first member of a new series of 11-heteropoly-tungstic acids with mainly positive central ions, has been isolated. The acid and a number of its salts have been described and analysed, and a reaction mechanism has been suggested to account for their formation. In all, three methods of preparation have been studied, one or more of which can be used to determine with reasonable certainty whether any metallic ion forms a heteropoly-tungstate and, if so, to which series it belongs. A rapid and economical method for the preparation of metatungstic acid and of sodium metatungstate has also been indicated.

ALTHOUGH the field of heteropoly-molybdate and heteropoly-tungstate preparation, apart from subsidiary valency states of the central ion, has been very fully investigated since the discovery by Marignac of the tungstosilicates, no clear picture of the mechanism of formation of these

compounds can be derived from a study of the relevant literature. Whether a particular ion is capable of heteropoly-molybdate or -tungstate formation depends on two factors, the structural and the chemical. There is at present no means of predicting whether an ion can form part of a stable condensed anion containing between 6 and 12 MoO_3 or WO_3 residues; the question must be answered by experiment. The chemical factors are more amenable, and some indication of their nature can be obtained from consideration of the equilibrium between molybdate or tungstate ions and hydrogen ions in aqueous solution.

Acidification of alkali molybdate or tungstate solutions, provided that these are not too concentrated and that the temperature is kept near the boiling point to allow equilibrium to be more rapidly attained, leads eventually (at pH values near 3) to almost quantitative formation of alkali metamolybdate or metatungstate. On further acidification (to pH < 1), molybdic acid passes through its isoelectric point and forms cationic complexes with the anion of the acid used in acidification; the metatungstate ion, on the other hand, behaves as a stable ion, giving rise to metatungstic acid, $H_6[H_2W_{12}O_{40}]$,aq. This acid is the hypothetical parent of all 12-heteropoly-tungstic acids, these being derived from it by replacement of hydrogen ion by other anions, or, as the sequel shows, by cations. No comparable stable form of molybdic acid is known (apparently the $Mo_{12}O_{40}$ group is stable only in presence of co-ordinated negative ions), and to this is doubtless due the smaller number and generally lower stability of the heteropoly-molybdic acids. Heteropoly-compounds containing between 11 and 8 MoO_3 or WO_3 residues to each central atom are either derived from 12-acids by hydrolysis, or represent the upper attainable limit of saturation consistent with stability.

If another ion is present along with molybdate or tungstate during acidification, it may replace hydrogen ion in the condensed molybdate or tungstate nucleus, thus giving rise to a heteropoly-compound. Whatever the details of preparation may be, all heteropoly-acids are formed in this way. Where the central ion is negative, *e.g.*, PO_4^{3-}, preparation of the heteropoly-acid is a simple matter, stoicheiometrical relations being of minor consequence, so long as the minimum quantity of central ion demanded by the formula is present. Where the central ion is positive, excess over the stoicheiometrical proportion may lead to decomposition, through secondary precipitation reactions, of the heteropoly-compound already formed.

The rule by which the correct relative proportions of positive ion and molybdate or tungstate ion may be determined is simple, and follows from what has already been stated. With sodium paramolybdate or paratungstate as initial substance (the usual material for heteropoly-compound preparations), and complete hydrolysis of the added salt containing the required positive ion being assumed, saturation is complete when the acid derived from hydrolysis is just sufficient to convert the molybdate or tungstate from the para- into the meta-form. The process is thus an indirect acidification of paramolybdate or paratungstate solutions to an extent which, an equivalent amount of mineral acid being used for the purpose, would give the meta-form. In general, if no heteropoly-compound is formed, and if the equilibrium is not disturbed by secondary precipitation, which usually takes place in such cases, the final product is sodium metamolybdate or metatungstate. If the metatungstic acid, obtained from the latter by extraction with ether and hydrochloric or sulphuric acid, shows no trace of the originally added ion, the evidence for heteropoly-compound formation is almost certainly negative.

If the salt formed is of the higher series, with 8 or more MoO_3 or WO_3 residues, and if no secondary precipitation has taken place during saturation, the solution will have a pH similar to that of an equivalent metamolybdate or metatungstate solution, and the free heteropoly-acid may be isolated as its ether addition compound by extraction with ether and sulphuric or hydrochloric acid, or, though this is less conclusive, the solution may be used for preparation of salts by double decomposition. If the solution, however, has a pH similar to that of the original paramolybdate or paratungstate solution, only a 6-heteropoly-molybdate or -tungstate is present, again on condition that there has been no secondary precipitation during saturation. Since the alkali salts of the 6-series are usually of low solubility in water, they normally crystallise from solution on cooling. Where no heteropoly-compound is formed, precipitation of double metal–alkali metal paramolybdates or paratungstates usually takes place from an early stage of the saturation, though such precipitation must not be taken as conclusive without further trial by the alternative methods of saturation described below.

Since boiling sodium paratungstate solutions of the concentration used have a pH $> 6{\cdot}4$, it follows that all cations whose hydroxides precipitate (or begin to precipitate) at this value of pH, or below it, are potentially capable of heteropoly-tungstate formation. Comparable sodium paramolybdate solutions have a lower pH (*ca.* 4·8). Their hydrolytic capacity is thus substantially less, and so far it has not been found possible to prepare a heteropoly-molybdate of

type higher than the 6-type, with a positive central ion. An approximate relation between heteropoly-molybdates and heteropoly-tungstates having the same positive central ion is that, when the heteropoly-molybdate is a 6-compound, as with Fe^{3+}, Al^{3+}, Cr^{3+}, the corresponding heteropoly-tungstate is an 11- or 12-compound, and *vice versa*. In the case of Mn^{3+}, structural factors must also be involved, since, while tungsten gives an 11-heteropoly-compound, molybdenum reacts only with quadrivalent manganese, and tungsten does not. It is obvious that with cations such as Ag^{1+}, Hg_2^{2+}, Hg^{2+} and Pb^{2+}, whose normal, para-and meta-molybdates are all of low solubility, heteropoly-molybdate or -tungstate formation is scarcely possible, because of limits set by secondary ionisation of any complex formed, and by the restricted range of methods of preparation, though the pH relations for salt hydrolysis are favourable.

In the sequel, alternative methods of preparation are described which can be applied as tests of heteropoly-compound formation in such and similar cases, and for use when a weakly basic cation, *e.g.*, Bi^{3+} or Sb^{3+}, can only be retained in solution by an excess of mineral acid, which would preferentially give rise to metamolybdate or metatungstate before the desired hydrolysis was under way. Many anomalous heteropoly-compounds, particularly of tungsten, with positive central atoms, are described in the literature, and it is intended, on the basis set out, to establish some degree of order in this field, on the purely chemical side at least.

The only 6-heteropoly-tungstates so far described are the 6-tungstoferrates (Rosenheim and Schwer, *Z. anorg. Chem.*, 1914, **89**, 234). These belong to a series which, for molybdenum, includes the 6-molybdo-ferrates, -chromates, -aluminates, and -rhodates. As Rosenheim (Gmelin, "Handbuch," Syst. Nr. 54, 396; Abegg, "Handbuch," Vol. 4, Part 1, ii, p. 1050) has given varying accounts of the preparation and properties of the 6-tungstoferrates, the matter was reinvestigated as a preliminary to the preparation of the chromium and aluminium analogues. These 6-heteropoly-compounds are of paratungstate or paramolybdate type, having a tervalent central atom; the 6-tungstoferrates derive from a hypothetical acid $H_3(FeW_4O_{16})$,aq. Since the molybdenum analogues are appreciably dissociated into their components in aqueous solution, it would seem unlikely that 6-tungstoferric acid could exist in the free state. The sodium salts of these compounds are prepared by saturation of boiling sodium paratungstate or paramolybdate solutions with the nitrate or chloride of the tervalent metal. From the solution of the sodium salt of the 6-heteropoly-compound thus obtained, the other salts are prepared by double decomposition. Although the alkali paramolybdates are correctly represented by the general formula $3R_2O,7MoO_3$,aq., the formulation of the alkali paratungstates is less certain. Analytical results favour the formula $5R_2O,12WO_3$,aq., but, on grounds of general resemblance between molybdenum and tungsten compounds, the $3R_2O,7WO_3$,aq. formulation seems preferable. Anderson's suggestion (*Nature*, 1937, **140**, 850) that the paramolybdates and paratungstates are in fact $R_6[Mo(MoO_4)_4]$,aq. and $R_6[W(WO_4)_4]$,aq., emphasises in particular the very marked differences in chemical behaviour between alkali paratungstates and metatungstates, the latter being undoubtedly dodecatungstates.

Aqueous solutions of sodium paratungstate show a marked rise in pH on boiling, the increased alkalinity persisting after cooling. It was suggested by von Knorre (*Ber.*, 1885, **18**, 2363) that this behaviour is due to hydrolytic fission of the paratungstate ion into normal tungstate and metatungstate ions, $3(3Na_2O,7WO_3) \rightleftharpoons 5Na_2WO_4 + 4(Na_2O,4WO_3)$, the rise in pH being due to the normal tungstate. Rosenheim and Wolff (*Z. anorg. Chem.*, 1930, **193**, 54) have isolated metatungstates by double decomposition from such sodium paratungstate solutions, the equilibrium in which is certainly complex. Souchay (*Ann. Chim.*, 1943, **18**, 87) has shown that metatungstate ion cannot exist at pH values similar to those prevailing in sodium paratungstate solutions. The behaviour of metatungstate ion alone in buffer solutions of pH 6·5 does not, however, invalidate von Knorre's hypothesis, since in sodium paratungstate solutions the metatungstate ion is derived from paratungstate itself, and would be regenerated at once if destroyed. Experience shows that pH alone, although distinctive for each separate species of tungstate, gives little indication of the relative proportions of each in solutions whose history is not known.

In a series of studies of the neutralisation curves of Na_2MoO_4 with hydrochloric acid, Byé (*Bull. Soc. chim.*, 1942, **9**, 360; 1943, **10**, 239; *Ann. Chim.*, 1945, **20**, 463) has shown that in solutions of constant ionic strength (M. in NaCl) breaks are obtained at points corresponding to para-, tri-, and tetra(or meta)-molybdate for solutions 0·01—0·02M. in $Na_2MoO_4,2H_2O$. More concentrated solutions show extremely complex equilibria, the complexity increasing with concentration, while in very dilute solutions (0·0003M.) only the simple MoO_4^{2-} ion can be recognised. In dilute solutions, in the absence of added sodium chloride, the neutralisation curve is continuous, with a marked fall in pH only at the tetramolybdate stage, the condensation

to more acidic multivalent ions masking the pH changes corresponding to para- and tri-molybdate. Doucet and Carpéni (*Bull. Soc. chim.*, 1947, **14**, 496) found the isoelectric point for MoO_3,aq. to be at pH 0·9; at lower pH values molybdenum is present as a cation MoO_2^{2+} or MoO^{4+}. The change from normal molybdate to cationic complex is thus continuous in dilute solution, possibly accounting for the fact that no metamolybdic acid corresponding to meta-tungstic acid has yet been isolated. Byé (*Ann. Chim.*, 1945, **20**, 504) has assumed that an equilibrium of the von Knorre type is set up in paramolybdate solutions: $3Mo_7O_{24}^{6-} \rightleftharpoons 4Mo_4O_{13}^{2-} + 5MoO_4^{2-}$, moving to the left in concentrated solutions and to the right on dilution, an ion $Mo_6O_{20}^{4-}$ appearing between the para- and the tetra-molybdate stage.

Much work has been done on the neutralisation curves of $Na_2WO_4.2H_2O$, but with conflicting results. Tungstic acid, unlike molybdic acid, does not form cationic complexes, and its isoelectric point is at considerably higher pH values. On acidification of solutions of Na_2WO_4 at room temperature white hydrated tungstic acid separates, redissolving in the residual tungstate up to the point where paratungstate formation is complete: pH *ca.* 6·4. Beyond this point, depending on the concentration of the solution, either the precipitate of $WO_3.xH_2O$ becomes permanent or, in more dilute solutions, the tungstic acid remains in colloidal suspension, being precipitated only after keeping. In neither case does the whole of the tungstate ion remain to take part in the equilibrium, and neutralisation curves obtained under these conditions vary considerably, and in no case represent a true equilibrium between tungstate and hydrogen ions. If the acidification is carried out at the boiling point, however, no separation of tungstic acid occurs, and the pH of the solution can be brought below 2 without precipitation of $WO_3.xH_2O$. At pH values below 3·6 the solution is stable to strong acidification, and from it the ether addition compound of metatungstic acid can be obtained in quantitative yield. Acidification of alkali tungstate solutions at higher temperatures therefore finally gives metatungstate, and the equilibrium, as with molybdate solutions at ordinary temperatures, is homogeneous throughout, provided that, as emphasised by Doucet and Carpéni (*loc. cit.*, p. 486), time is allowed for equilibrium to be attained at each stage of acidification. According to Souchay (*loc. cit.*, p. 69), unless the ionic strength of the solution is kept constant (μ. or 2μ. in sodium chloride) during acidification, the neutralisation curve obtained shows no break corresponding exactly to para-tungstate, but to metatungstate only, the change in $[H^+]$ due to more acid salt formation being concealed or displaced by that caused by formation of polytungstate ions. Boiling of the solution after each addition of acid, although it gives higher pH values at each stage, still gives only the break at metatungstate, with nothing intermediate. Vallance and Pritchett's titration curves (*J.*, 1934, 1586) are exceptional in this respect, the formation of paratungstate being clearly shown, owing no doubt to the high concentrations of sodium tungstate and acid used. Preliminary experiments on the neutralisation of 0·022M-Na_2WO_4 with 0·1M-HCl, the tungstate solution being kept at the boiling point until, after cooling, a maximum value of pH was obtained at each stage of acidification (8—12 hours), show a well-defined break in the neutralisation curve at the paratungstate stage (pH *ca.* 6·7), a region of constant pH round the tritungstate stage (though no $Na_2O,3WO_3$ could be isolated from solution), and an abrupt break from pH *ca.* 5·8 to pH *ca.* 3·9 at the metatungstate stage. Na_2MoO_4 solution (0·022M.), similarly treated, showed no marked break in the neutralisation curve either in hot or in cold solution, even at the tetra-molybdate stage. The molybdate pH values were 0·1—0·2 pH unit higher for the heated solution (after cooling) than for the corresponding stage of acidification in cold solution. Beyond $Na_2O,4{\cdot}2WO_3$ and $Na_2O,4{\cdot}2MoO_3$ the titration curves were coincident. The successive steps in the tungstate neutralisation in hot solution would doubtless be better defined in solutions of constant ionic strength, as used by Byé and Doucet and Carpéni (*locc. cit.*), but the essential point, as regards the present investigation, is the quantitative formation of metatungstate by the slow acidification of boiling normal tungstate or paratungstate solutions with an acid sufficiently strong to bring the final pH below 4, and its bearing on the interaction of paratungstate solutions and solutions of metallic salts capable of yielding hydrogen ion by hydrolysis.

The mechanism of 6-heteropoly-molybdate formation, by saturation of paramolybdate solutions with solutions of metallic salts, is obscure. The formation of ferric pentamolybdate, $Fe_2O_3.5MoO_3$,aq. (Marckwald, Diss., Basel, 1895), as a by-product of the saturation of $3Na_2O,7MoO_3$ solutions with aqueous ferric chloride suggests that hydrolysis of the ferric chloride gives rise in part to products more acid than paramolybdate.

Saturation of boiling sodium paratungstate solutions with aqueous ferric nitrate gives a precipitate varying in composition between $Fe_2O_3.3{\cdot}3WO_3$,aq. and $Fe_2O_3.4{\cdot}3WO_3$,aq., dissolving readily in the residual paratungstate solution up to a fairly definite point, at which it becomes permanent. If sodium paratungstate, derived by acidification from 6 moles of $Na_2WO_4.2H_2O$ is

used, precipitation becomes permanent when about 0·75 mole of ferric nitrate nonahydrate has been added. Saturations carried beyond this point give a mother-liquor much poorer in iron, as is to be expected from the composition of the precipitate. There is thus a fairly definite optimum point in the saturation. The precipitate dissolves readily and almost completely in boiling sodium paratungstate solutions to give a solution of similar properties to that from which it originally separated, the process resembling the conversion of sodium paratungstate into metatungstate by saturation of a boiling solution of the former with $WO_3.xH_2O$, the pH of the solution falling from above 6·4 to between 3 and 4. At the point in the saturation of sodium paratungstate with ferric nitrate where precipitation becomes permanent, the pH of the solution has also fallen to between 3 and 4, and acidification no longer precipitates $WO_3.xH_2O$. To convert 6 moles of $Na_2WO_4.2H_2O$ from $3Na_2O,7WO_3$.aq.(para-) into $Na_2O,4WO_3$.aq.(meta-) without loss of tungsten, requires 2·14 equivs. of acid. Complete hydrolysis of the added ferric nitrate being assumed, 2·14 equivs. of acid would be given by 0·71 mole, approximately the amount required for optimum saturation of the sodium paratungstate used. In the saturation of sodium paratungstate with ferric salt it appears that the maximum iron content of the solution is attained when, complete hydrolysis of the ferric salt being assumed, the hydrogen ion set free is just enough to convert the whole of the paratungstate into metatungstate. This stoicheiometric relation has been found to apply generally to saturations of sodium paratungstate solutions with solutions of metallic salts, provided no secondary precipitation takes place. The solutions then have a pH value similar to that of an equivalent sodium metatungstate solution, and are similarly stable to strong acidification. It may be that, in the boiling paratungstate solution (a hydrolytic equilibrium of the von Knorre type being assumed) the normal tungstate acts both as hydrolytic agent and as precipitant for the ferric salt, and that the ferric ion in part replaces hydrogen ion in the spontaneous change of paratungstate ion $[W(W_6O_{21})]^{6-}$ to metatungstate ion $[H_2W_{12}O_{40}]^{6-}$, the paratungstate merely providing the material for these reactions. Saturation is complete when insufficient paratungstate remains to carry either reaction further. There is some indication that sodium metatungstate, on saturation with ferric hydroxide, gives identical products, but whether this is due to direct replacement of hydrogen ion by ferric ion in the metatungstate ion, or whether reversion to paratungstate forms an intermediate stage, is not certain.

Acidification of boiling sodium tungstate or paratungstate solutions, with an acid sufficiently strong to give a final pH between 3 and 4, gives quantitative conversion into metatungstate (von Knorre, *loc. cit.*). Here again it is possible that the acid merely converts the normal tungstate (the most alkaline component) into paratungstate, which again undergoes hydrolytic fission to normal tungstate and metatungstate, the cycle being repeated till finally only metatungstate remains. The reaction is thus not a simple displacement of the weak " tungstic acid " by a stronger acid, but represents the driving to virtual completion of a complex hydrolytic equilibrium present from the first. Preparation of heteropoly-tungstates by saturation of sodium paratungstate solutions must therefore be carried out slowly to keep pace with the hydrolytic displacement, and neglect of this precaution, especially in saturations with metallic salts, may lead to failure in the isolation of these compounds. Absence of paratungstate, corresponding to complete saturation, cannot be safely assumed even at pH values below 4, unless saturation has been extended over several hours. Even in acidified molybdate solutions equilibrium is only slowly reached, though stable values of pH may be obtained almost at once (Doucet and Carpéni, *loc. cit.*, p. 486).

Almost all methods for the preparation of heteropoly-tungstates depend on saturation of boiling sodium paratungstate solutions with a compound containing the ion which is to form the central ion in the heteropoly-tungstate anion, and, if the von Knorre hypothesis is accepted, all such preparations must contain more or less sodium metatungstate, the amount varying inversely with rapidity of formation of the heteropoly-tungstate. This applies even more to the use of ammonium paratungstate for such preparations, since it passes spontaneously into metatungstate when its solutions are boiled. Heteropoly-tungstic acids derived from such saturations will therefore be accompanied by more or less metatungstic acid.

The potassium and ammonium 6-tungstoferrates described by Rosenheim and Schwer (*loc. cit.*) could not be reproduced, no definite compounds separating when the product of saturation was treated with concentrated potassium chloride or ammonium chloride solution. Guanidine hydrochloride gave yellow microcrystalline products of variable composition, all containing more tungsten than required by the 6-formulation. The pH of the saturation products and their stability to strong acidification showed that compounds of paratungstate type could only be present in small amount, if at all.

Treatment of the products of saturation with ether and 6*N*-sulphuric acid (Drechsel, *Ber.*, 1887, **20**, 1452) gave a typical heteropoly-acid–ether addition compound. Analyses of specimens from identical saturations showed a widely variable iron content. From the relative proportions of sodium paratungstate and ferric nitrate used in the saturations, Fe : W could have a maximum value of 8·5. Values obtained ranged from 14 to 21 and above. It was assumed, for the reasons already given, that the high proportion of tungsten was due to the presence of metatungstic acid, derived from sodium metatungstate formed furing the saturation with ferric nitrate.

The thermal stability of metatungstic acid is low (cf. Sobolew, *Z. anorg. Chem.*, 1896, **12**, 30), and by making use of this property it was found possible to eliminate this acid, leaving tungstoferric acid as final product. This substance, recrystallised from water, and air-dried, has a composition agreeing with the empirical formula $Fe_2O_3.22WO_3.50H_2O$. From its stability it might be expected to belong to the limiting series and be an analogue of 12-tungstoboric acid, $B_2O_3.24WO_3.53H_2O$, but the results of analysis of the free acid and its salts, as also of those of its homologues (see Part II), agree better with the 11-formulation. It is thus the first member of a new series of 11-heteropoly-tungstic acids with positive or mainly positive central ions, and may be described as 11-tungstoferric(III) acid. It retains $5H_2O$ at temperatures up to 240°, and gives a series of salts of which the ammonium and barium salts are 10- or 9-basic, the cæsium and silver salts 9-basic, and the sodium, potassium, and guanidine salts, 8-basic. As with many other heteropoly-acids, the mercurous salt is anomalous, being approximately 16-basic, but its insolubility as compared with the other salts suggests that it is a basic salt (cf. Souchay, *Bull. Soc. chim.*, 1942, **9**, 289), and does not indicate a true basicity. Potentiometric neutralisation with sodium hydroxide shows a basicity of *ca.* 9·2, as does also neutralisation with barium carbonate, and conductometric titration with potassium or ammonium hydroxide gives a value of *ca.* 10·1. The acid appears therefore to be 10-basic, and may be formulated as, $5H_2O,Fe_2O_3.22WO_3.45H_2O$. Its formula on the Rosenheim–Miolati basis would be either

$$H_5\left[Fe\begin{matrix}(W_2O_7)_4\\OH\end{matrix}\right]-W_2O_7-\left[\begin{matrix}(W_2O_7)_4\\OH\end{matrix}Fe\right]H_5 \quad \text{or} \quad H_{10}\left[Fe\begin{matrix}(W_2O_7)_4\\ \diagdown\\ W_2O_7\end{matrix}\begin{matrix}(W_2O_7)_4\\ \diagup\\ \end{matrix}Fe\right]$$

neither of which agrees with its basicity as found experimentally. Wells (" Structural Inorganic Chemistry," p. 345) has suggested (following Pauling) alternative binuclear formulæ for the tungstophosphoric acids containing less than 12 tungsten atoms to each PO_4^{3-}. These formulæ assume the presence of two central ions in a structure based possibly on the cubo-octahedron, and give the general anionic form as $[P_2W_yO_{3y+6}]^{6-}$. By analogy the ion of 11-tungstoferric(III) acid would be $[Fe_2W_{22}O_{74}]^{10-}$, in agreement with the basicity as experimentally determined; the anhydrous acid would be $H_{10}[Fe_2W_{22}O_{74}]$. The Rosenheim–Miolati formulations imply that 11-tungstoferric acid is the hydrolysis product of a higher acid, presumably 12-tungstoferric acid, but its stability is much higher than that of 10(or 11)-tungstosilicic acid or 11-tungstophosphoric acid, and the preparation of the acid and of its salts has been carried out, as far as possible, under conditions unfavourable to hydrolysis. No evidence has been obtained, for either 11-tungstoferric acid or its homologues, of the presence of salts derived from a 12-acid, apart from the uncertainties of analysis. 11-Tungstoferric(III) acid appears to resist reduction by sulphurous acid to an 11-tungstoferric(II) acid, possibly because ferrous iron gives only a 6-heteropoly-tungstate, which oxidises rapidly in air to give indefinite products resembling the by-products in the tungstoferrate preparation. 11-Tungstoferric acid is stable in the solid state, only a trace of water-insoluble material separating on long keeping. Aqueous solutions are equally stable.

Experimental.

$Na_2WO_4.2H_2O$ (56·2 g.), dissolved in water (300 ml.) was converted into $3Na_2O,7WO_3$ by addition of *N*-nitric acid (194·4 ml.). The boiling, mechanically stirred solution was saturated dropwise during 20—24 hours with aqueous ferric nitrate solution (8·6 g. of nonahydrate in 400 ml.). This is 5% in excess of the amount required to give 60·8 ml. of *N*-nitric acid on complete hydrolysis, being the volume of *N*-nitric acid necessary to convert the paratungstate present into metatungstate. This excess was found to be desirable, owing to slight precipitation losses during saturation. Ferric chloride was not used because of the risk of its extraction by ether in the subsequent stages of preparation. Ferric sulphate was found to be unsatisfactory because of loss of iron as basic sulphate through incomplete hydrolysis. The yellow solution (described as " colourless " by Rosenheim, Abegg, " Handbuch," *loc. cit.*, p. 1050) was concentrated to 200 ml. and kept overnight at 6° to allow unchanged paratungstate to separate. After filtration, ether extraction by Drechsel's method (*loc. cit.*) gave the golden-yellow ether addition compound of 11-tungstoferric acid, mixed with that of metatungstic acid; 6*N*-sulphuric acid was used for acidification in this process, no cooling being necessary.

Isolation of 11-*Tungstoferric*(III) *Acid.*—The ether addition compound was freed from entrained mother-liquor by dropping it through two or three portions of fresh ether. On dilution with water the

ether separated, and was removed by an air current. The aqueous solution was evaporated to dryness on the steam-bath, the residue was extracted with water, and the separated tungstic acid filtered off. The filtrate was again evaporated to dryness on the steam-bath, the process being repeated till separation of tungstic acid became slow. The dry residue was then baked at 120—130° for 4 hours, the residue being extracted with water, as before, and filtered. This process was repeated until separation of tungstic acid practically ceased. The tungstic acid residues contained only traces of iron, being derived almost entirely from the metatungstic acid. The final aqueous extract was partly concentrated on the steam-bath, then *in vacuo* over sulphuric acid. 11-*Tungstoferric acid* separated as a yellow crystalline mass, which was drained on a sintered filter and dried between filter-papers (yield variable, but averaging 30%) (Found : Fe_2O_3, 2·53; WO_3, 82·89; H_2O, 14·58. $Fe_2O_3,22WO_3,50H_2O$ requires Fe_2O_3, 2·59; WO_3, 82·80; H_2O, 14·62%). On dehydration, constant weight was attained between 180° and 240°, $35H_2O$ being lost at 110° and a further $10H_2O$ between 110° and 180° (Found : loss at 180°, 13·12. $Fe_2O_3,22WO_3,50H_2O$ requires $45H_2O$, 13·16%). The residue of anhydrous 11-tungstoferric acid was almost completely soluble in water, indicating little decomposition (less than 2% insoluble after 100 hours at 240°), and rapidly regained weight on exposure to moist air. For comparison the composition of the possible 12-acid, $Fe_2O_3,24WO_3,54H_2O$, would be : Fe_2O_3, 2·38; WO_3, 83·16; H_2O, 14·52%; and loss of 13·12% at 180° would leave $5·5H_2O$.

Properties. The acid is very soluble in water (408 g. of 50-hydrate per 100 g. of water at 19°, density of solution 2·76) and crystallises only in aggregates, with occasional octahedral outlines; pH of 0·0014M-solution, 1·82 (cf. Rosenheim and Breuer, *Z. anorg. Chem.*, 1915, **93**, 284, for pH values for other heteropoly-acids); the acid has *d* 4·28, m. p. *ca.* 43°. It is stable to strong acids or bases in cold solution, and is decomposed on heating with separation of tungstic acid or ferric hydroxide, and therefore does not cause interference in the analytical separation of iron from tungsten by digestion with hydrochloric acid and cinchonine. Potentiometric titration with sodium hydroxide gave an equivalent weight *ca.* 670, the basicity of the acid being 9·2 on the assumed M.W. of 6162·74, the maximum value of dE/dV occurring near pH 5·7.

Further Methods of Preparation.—Two other methods of preparation of 11-tungstoferric acid were used for exploratory purposes.

(1) *Ferric hydroxide method.* To a sodium paratungstate solution, prepared as described above from 56·2 g. of $Na_2WO_4,2H_2O$ by addition of 194·4 ml. of N-nitric acid, was added well-washed ferric hydroxide, prepared from 10 g. of hydrated nitrate by precipitation with aqueous ammonia. The boiling, mechanically stirred mixture was acidified during 20—24 hours with an approx. 0·1N-nitric acid solution containing 64 ml. of N-acid (5% excess : cf. p. 2369). On completion of saturation, the solution was concentrated to 200 ml., filtered, and kept overnight at 0°. After separation of any unchanged paratungstate which had been deposited, the filtrate was extracted as before with ether and 6N-sulphuric acid. The tendency to emulsification, due to traces of WO_3,xH_2O derived from residual paratungstate, was more marked with these preparations, direct saturation with ferric nitrate being preferable, but an identical ether addition compound of 11-tungstoferric acid, mixed with metatungstic acid, was obtained. This method of saturation is of value, however, in those cases where, as with Bi^{3+} or Mn^{2+} salts, the metal ion can only be retained in solution by a substantial excess of acid, which would tend to give metatungstate as main product, or where the metal paratungstate is so sparingly soluble that addition of the salt gives double decomposition only.

The residue of ferric hydroxide contained substantial amounts of tungsten, and dissolved almost completely in water to give a dark red solution which, after sedimentation or centrifuging, was only perceptibly turbid, and remained unchanged for long periods. Evaporation to dryness on the steam-bath gave a dark red vitreous residue which again dissolved completely in water, and the process could be repeated many times. Addition of sodium chloride to the solution caused immediate and almost complete precipitation of a reddish-brown solid resembling ferric hydroxide. Air-dried specimens had an average composition represented by $3Na_2O,7WO_3,4·3Fe_2O_3,31H_2O$, the pH of a 2·25% aqueous solution being 6·56. Other oxides and hydroxides have been found to behave similarly. Saturation of ammonium paratungstate solutions with metallic hydroxides has been used by various workers to prepare heteropoly-tungstates, and there can be little doubt that, electrolytes being virtually absent in such cases, the products isolated were contaminated with peptized hydroxides, as described above, and showed an excessively high metal oxide content.

(2) *Metatungstate method.* A solution of $Na_2O,4WO_3$ aq. was prepared by following the same procedure as described above, but omitting the ferric hydroxide and shortening the time of addition of the second portion of nitric acid to 4—5 hours. To this solution, heated to boiling and mechanically stirred, was added, as before, freshly precipitated ferric hydroxide prepared from 10 g. of hydrated nitrate. The reaction is very slow and saturation was continued for about 50 hours. The solution was concentrated to 200 ml., filtered, and extracted with ether and 6N-sulphuric acid. Analysis of the ether addition compound showed that about 10% of tungstoferric acid was present. The yield could probably be improved by using successive portions of fresh ferric hydroxide, since this ages rapidly in boiling solution. The residue of ferric hydroxide was again almost completely soluble in water, and gave on sedimentation and evaporation a dark red solid similar to that described above, and containing substantial amounts of tungsten.

According to Souchay (*loc. cit.*, p. 84) only sodium paratungstate solutions, freshly prepared by acidifying alkali tungstate, are active in heteropoly-acid formation, losing activity in a few hours, while paratungstate or metatungstate solutions prepared from the crystalline salts are almost inactive. There may thus be a decrease in reactivity of the metatungstate solution as well as of the ferric hydroxide during the saturation, accounting for the relatively poor yield of heteropoly-acid.

Metatungstic Acid.—The solution of sodium metatungstate described above, on extraction with ether and 6N-sulphuric acid, gives a quantitative yield of the ether addition compound of metatungstic acid,

and from this sodium metatungstate can be obtained by neutralisation with sodium hydroxide to pH 3·6 and concentration to crystallisation. This method of preparation is superior to the tedious and wasteful process of saturating solutions of sodium tungstate or paratungstate with freshly precipitated tungstic oxide, much of the added tungsten being lost as insoluble alkali polytungstate. The low stability of metatungstic acid in aqueous solutions leads to considerable loss in isolation in solid form, no matter from what source it is derived.

On addition of aqueous barium chloride to a solution of sodium metatungstate, a small amount of barium tritungstate, $BaO,3WO_3,6H_2O$ (Scheibler, *J. pr. Chem.*, 1860, **80**, 204) separates in microcrystalline form before the barium metatungstate. This happens with sodium metatungstate, whether prepared by saturation of paratungstate with WO_3,xH_2O or by neutralisation of aqueous metatungstic acid with sodium hydroxide. If the formation of tritungstate were due to disproportionation, hydrogen ions should be set free. Potentiometric and conductometric titration of sodium metatungstate solutions from both sources with aqueous barium chloride shows no apparent fall in pH, or rise in conductivity. It seems probable that the tritungstate (averaging 2—3% of the total) is constantly present in sodium metatungstate, representing the not quite complete conversion of paratungstate into metatungstate by the hydrolytic displacement assumed by von Knorre.

Salts of 11-*Tungstoferric*(III) *Acid.*—*Sodium salt.* This *salt* was obtained by neutralising 11-tungstoferric acid with sodium hydroxide to pH 4·0 (checked potentiometrically on aliquot portion of solution) and concentrating the solution; it was a pale yellow, slightly efflorescent solid, melting below 50°, very soluble in water and crystallising only in aggregates (Found: Na_2O, 3·82; Fe_2O_3, 2·52; WO_3, 79·52; H_2O, 14·15. $4Na_2O,Fe_2O_3,22WO_3,50H_2O$ * requires Na_2O, 3·87; Fe_2O_3, 2·49; WO_3, 79·59; H_2O, 14·05%). It retains *ca.* $2H_2O$ at 200°; the pH of a 0·0014M-solution is 5·28.

Ammonium salt. This *salt* can be prepared either by neutralising the free acid with aqueous ammonia (potentiometrically checked as for the sodium salt) or by saturating aqueous solutions of the acid with ammonium chloride; recrystallised from water, it forms pale yellow hexagonal prisms, usually in rosettes, but sometimes with long axes parallel in bundles [Found: $(NH_4)_2O$, 4·33; Fe_2O_3, 2·73; WO_3, 88·36; H_2O, 4·58. $5(NH_4)_2O,Fe_2O_3,22WO_3,15H_2O$ requires $(NH_4)_2O$, 4·49; Fe_2O_3, 2·76; WO_3, 88·09; H_2O, 4·66%]; *d* 4·714. The salt is anhydrous at 160° and decomposes from 170°; it is easily soluble in water and a 0·0014M-solution has pH 4·78.

The salt prepared by neutralisation is not homogeneous. On recrystallisation from water it gives a first fraction of yellow crusts, with higher ammonia content [Found: $(NH_4)_2O$, 7·28; Fe_2O_3, 2·80; WO_3, 81·89; H_2O, 8·03. $8(NH_4)_2O,Fe_2O_3,20WO_3,25H_2O$ requires $(NH_4)_2O$, 7·36; Fe_2O_3, 2·82; WO_3, 81·67; H_2O, 7·95%]. This may be a hydrolysis *product*. The later fractions are identical with the 10-basic salt, crystallising in the same form, but occasionally, from concentrated solutions, as deliquescent octahedra.

Potassium salt. This *salt* was prepared by saturating an aqueous solution of the acid with potassium chloride; it is isomorphous with the ammonium salt, but rather less soluble in water; pH of 0·0014M-solution, 4·67 (Found: K_2O, 5·06; Fe_2O_3, 2·61; WO_3, 82·27; H_2O, 9·1. $4K_2O,Fe_2O_3,22WO_3,31H_2O$ requires K_2O, 6·08; Fe_2O_3, 2·58; WO_3, 82·34; H_2O, 9·01%).

Barium salts. There appear to be two *barium* salts. (i) That prepared by neutralising the acid with the carbonate and concentrating the solution crystallises in pale yellow, slightly deliquescent octahedra, *d* 4·452, readily soluble in water (Found: BaO, 10·41; Fe_2O_3, 2·36; WO_3, 75·99; H_2O, 11·48. $4·5BaO,Fe_2O_3,22WO_3,43H_2O$ requires BaO, 10·26; Fe_2O_3, 2·37; WO_3, 75·85; H_2O, 11·52%); it retains *ca.* $2H_2O$ at 180°. (ii) Saturation of aqueous solutions of the acid with barium chloride gives a distinctive tetragonal form, pale yellow, usually twinned, *d* 4·734, and stable in air (Found: BaO, 11·69; Fe_2O_3, 2·46; WO_3, 76·71; H_2O, 9·24. $5BaO,Fe_2O_3,22WO_3,34H_2O$ requires BaO, 11·55; Fe_2O_3, 2·41; WO_3, 76·83; H_2O, 9·22%). This salt is apparently 10-basic and would be formulated as $Ba_5(Fe_2W_{22}O_{74}),34H_2O$. Since barium chloride is tenaciously held by barium salts of heteropoly-acids, the higher barium content may be due to this cause, the two salts being 9-basic, but different hydrates.

Cæsium salt. Prepared from aqueous solutions of the free acid and cæsium chloride, this very sparingly soluble *salt* crystallised from hot water in pale yellow slender prisms, isomorphous with the ammonium salt (Found: Cs_2O, 18·5; Fe_2O_3, 2·36; WO_3, 75·60; H_2O, 3·64. $4·5Cs_2O,Fe_2O_3,22WO_3,14H_2O$ requires Cs_2O, 18·70; Fe_2O_3, 2·35; WO_3, 75·23; H_2O, 3·72%); it retained *ca.* $1H_2O$ at 180°. Recrystallisation apparently causes some hydrolysis, and it is difficult to obtain well-defined crystals.

Guanidine salt. Prepared from aqueous solutions of the acid and guanidine hydrochloride, this *salt* formed pale yellow leaflets, sparingly soluble in water [Found: $(CN_3H_6)_2O$, 9·14; Fe_2O_3, 2·54; WO_3, 84·72; H_2O, 3·61. $4(CN_3H_6)_2O,Fe_2O_3,22WO_3,12H_2O$ requires $(CN_3H_6)_2O$, 9·04; Fe_2O_3, 2·65; WO_3, 84·72; H_2O, 3·59%]; it retains $5H_2O$ at 200°.

Silver salt. The *silver* salt, prepared from aqueous solutions of the acid and silver nitrate, formed pale yellow prisms, isomorphous with the cæsium and potassium salts (Found: Ag_2O, 15·76; Fe_2O_3, 2·33; WO_3, 76·47; H_2O, 5·58. $4·5Ag_2O,Fe_2O_3,22WO_3,21H_2O$ requires Ag_2O, 15·60; Fe_2O_3, 2·39; WO_3, 76·36; H_2O, 5·66%). It is sparingly soluble in water, but crystallises out only slowly; it dissolves completely in dilute nitric acid without separation of tungstic oxide.

Mercurous salt. Prepared from aqueous solutions of the acid and the nitrate, the *mercurous* salt formed a pale yellow microcrystalline solid, insoluble in water, completely soluble in dilute nitric acid (Found: Hg_2O, 38·52; Fe_2O_3, 1·84; WO_3, 56·73; H_2O, 2·91. $6Hg_2O,Fe_2O_3,22WO_3,14H_2O$ requires Hg_2O, 37·71; Fe_2O_3, 1·83; WO_3, 56·48; H_2O, 2·85%); it rapidly darkens on exposure to light, becoming almost black, and is probably a basic salt.

* This salt can be formulated as $Na_2H_6[Fe_2W_{22}O_{74}],49H_2O$, and the other salts described can be based on the same complex ion.

Analysis.—This has been based, wherever possible, on ignition followed by fusion with sodium carbonate, the residue of ferric oxide being freed from tungstic oxide by double precipitation from hydrochloric acid solution with aqueous ammonia, followed by solution of the ignited and weighed ferric oxide in hydrochloric acid and precipitation of the remaining trace of tungstic oxide with cinchonine. Most of the ferric oxide residues showed a trace of silica when heated with sulphuric and hydrofluoric acids. Tungsten was determined as trioxide after precipitation with cinchonine hydrochloride; barium as sulphate, usually on a separate sample, the anion of tungstoferric acid being stable to dilute sulphuric acid. Potassium and cæsium were determined as chloroplatinates, sodium as triple salt with zinc uranyl acetate, ammonia by distillation into standard acid, and guanidine by micro-combustion (J. C.). Silver and mercury were determined by thiocyanate titration after decomposition of the salts with nitric acid. The average value of $Fe_2O_3 : WO_3$ obtained is more nearly 1 : 23 than the 1 : 22 assumed in the formulæ already given, but no values exceeding 1 : 24 were obtained. Since traces of metatungstic acid might be expected to persist in spite of the drastic treatment of tungstoferric acid during isolation, and since small amounts of paratungstate separate in the double decompositions used to prepare the salts, the absence of values of $Fe_2O_3 : WO_3$ corresponding to a 12-tungstoferric acid suggests that the 11-formulation is the more probable. A final decision is, however, scarcely possible on analytical grounds alone.

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485. *Heteropoly-tungstic Acids and Heteropoly-tungstates. Part II. 11-Tungsto-aluminic, -chromic(III), and -manganic(III) Acids and their Salts.*

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Following the general methods outlined in Part I (preceding paper), three further 11-heteropoly-tungstic acids have been isolated, all with tervalent central ions. These are 11-tungsto-aluminic, -chromic(III), and -manganic(III) acid. The first two have been obtained in solid form, the third in solution only. From all three, salts have been prepared and characterised. A microscopical examination has been made of some of the salts to determine their principal optical constants. Some physical constants, including specific gravity and pH of aqueous solutions, have been noted.

By saturation of ammonium paratungstate solutions with aluminium hydroxide, Daniels (*J. Amer. Chem. Soc.*, 1908, **30**, 1846) obtained a colourless semi-transparent mass, assumed to be the ammonium salt of a tungstoaluminic acid, and from it prepared salts of metals by double decomposition. The free acid could not be isolated. Various heteropoly-tungstates of tervalent chromium and manganese, prepared by similar methods, have been described by Balke and Smith (*ibid.*, 1903, **25**, 1230), Daniels (*loc. cit.*), and Rogers and Smith (*ibid.*, 1904, **26**, 1745). These products were of variable composition, giving values of the ratio $R_2O_3 : WO_3$ between 1 : 9 and 1 : 12, and according to Rosenheim (Abegg's "Handbuch," Vol. 4, Part I, p. 1050) they were not definite compounds. Of the corresponding molybdenum compounds, only 6-molybdo-aluminates and -chromates are known, no compounds of higher series being formed. Tervalent manganese does not appear to form molybdate complexes, but quadrivalent manganese does, giving apparently a series of 9-molybdomanganates (Friedheim and Keller, *Ber.*, 1906, **39**, 4301).

Since electrolytes are virtually absent in saturations of ammonium paratungstate with metallic hydroxides, there is nothing to prevent extensive peptisation, and the products obtained by Daniels *et al.* undoubtedly contained an excess of metallic hydroxide, accounting for the low values of the ratio $R_2O_3 : WO_3$. The ready peptisation of ferric hydroxide in saturations of sodium paratungstate (Part I) confirms this view. Rosenheim (*loc. cit.*) is therefore justified in assuming that these tungsto-aluminates, -chromates, and -manganates are not definite compounds.

The solubilities of the alkali 6-heteropoly-tungstates and -molybdates are usually sufficiently low to permit the preparation of well-defined crystalline specimens by direct saturation of boiling alkali paratungstate or paramolybdate solutions with the appropriate metal nitrate or chloride. In some cases, however, where a very insoluble double alkali metal–metal paratungstate is formed, indirect methods must be used. The alkali salts of heteropoly-acids of higher series containing metallic substituents are much more soluble, and it is difficult to obtain authentic specimens from the complex mother-liquors derived from saturations. The isolation of the free heteropoly-acids is thus most desirable.

The general methods of preparation have been set out in Part I. Boiling sodium paratungstate solutions, with a pH $>6{\cdot}4$, are capable of precipitating aluminium, chromium, and manganic hydroxides from salts of the metals. Saturation with aqueous solutions of aluminium

nitrate runs smoothly, with virtually no secondary precipitation, the stoicheiometric basis being the same as that used in the preparation of 11-tungstoferric(III) acid. The pH of the saturated mother-liquor is <4 and the ether addition compound of 11-tungstoaluminic acid can be isolated by extraction with ether and 6*N*-sulphuric acid. Saturation of boiling sodium paratungstate solutions with aqueous chromium nitrate proceeds smoothly at first, but in the later stages precipitation of a green sodium chromium tungstate (approximately of paratungstate type) takes place. The pH of the saturated mother-liquor is between 5 and 6, and attempts at extraction with ether and 6*N*-sulphuric acid lead only to extensive precipitation of tungstic acid. It is necessary to acidify the hot mother-liquor with dilute nitric acid until the pH has fallen to 3. After cooling, extraction with ether and 6*N*-sulphuric acid can be carried out, though some emulsification is usual. The ready hydrolysis of manganic salts makes the use of dilute solutions of these as saturating agents scarcely practicable. Three methods of preparation have been used to obtain the saturated mother-liquor from which 11-tungstomanganic(III) acid can be extracted: (1) Saturation of boiling sodium paratungstate solution with an excess of freshly prepared manganic hydroxide, dilute nitric acid being slowly added in 10% excess of that required to convert the paratungstate into metatungstate. (2) Addition of solid potassium hexacyanomanganate(III), slowly and in small amounts to a boiling sodium paratungstate solution; hydrolysis to manganic hydroxide takes place at once, and this is readily taken up by the paratungstate. Because of the alkaline hydrolysis products of the hexacyanomanganate the solution must be acidified while hot with dilute sulphuric acid to bring the pH below 4 before extraction of the 11-tungstomanganic(III) acid with ether and 6*N*-sulphuric acid. (3) The best method is saturation of boiling sodium paratungstate solutions with small successive portions of an intimate mixture of manganous sulphate and potassium persulphate; this is similar to Friedheim and Keller's method (*loc. cit.*) for the preparation of the molybdomanganates. Oxidation of Mn^{2+} to Mu^{3+} takes place *in situ*, and the decomposition products of the persulphate give a mother-liquor of pH <4, from which, after removal of suspended manganese oxides, 11-tungstomanganic acid can be extracted without difficulty by Drechsel's method.

For reasons stated in Part I, the ether addition compounds obtained by Drechsel's method contain, in addition to tungsto-aluminic, -chromic, or -manganic acid, substantial amounts of metatungstic acid. From the first two acids this can be removed by repeated evaporation of their aqueous solutions, followed by baking, but the stability of the third acid is too low to withstand this treatment, and the acid has been obtained only in aqueous solution.

Analysis of the free acids and their salts shows that they are of similar composition to 11-tungstoferric(III) acid, the value of $R_2O_3 : WO_3$ approximating to 1 : 22. The four acids may thus be formulated as $R_2O_3,22WO_3,aq.$ or $H_{10}[R_2W_{22}O_{74}],aq$. The solubility of the acids in water is so high that only crystal aggregates can be obtained, though octahedral outlines appear on long keeping of concentrated solutions. Isomorphism is, however, shown by the salts, which vary in basicity between 8 and 10, and are all substantially hydrated. Tungstoaluminic acid and its salts are colourless, the chromic acid and its salts pale green or, exceptionally, violet, and the manganic acid and its salts intensely deep red. The ammonium, potassium, and barium salts are readily soluble in water, and crystallise well, but usually effloresce when kept, breaking down into microcrystalline powders. Isomorphism is very marked with the potassium and barium salts. The guanidine and silver salts are much less soluble, giving only small but well-defined crystals.

A microscopic examination has been made of some of the salts to determine their principal optical constants. The colour of the tungstomanganates is dependent on the colour of the crystal sections, varying from a light yellow in very thin sections to a dark red. Similarly, the tungstochromates appear colourless in thin sections and light green in thicker, while the tungstoaluminates are colourless. Typically octahedral cleavage is shown by nearly all crystal fragments, triangular views being of most frequent occurrence, although occasionally rectangular or hexagonal views are presented. Ammonium tungstoaluminate is uniformly isotropic and is therefore cubic. Ammonium tungsto-chromate and -manganate appear to exist as at least two different crystalline hydrates, one of which is cubic. Ammonium tungstomanganate, when dehydrated over phosphoric acid, is also cubic, but when exposed to the atmosphere it gradually develops weak polarisation colours when observed in polarised light. Ammonium tungstoferrate behaves similarly, the more hydrated form in each case being only weakly birefringent, and of lower refractive index than the dehydrated form. The guanidine salts of all three acids crystallise in rectangular prisms, which generally lie on the microscope slide so that the plane of the bisectrix is inclined at only a small angle to the vertical, thus allowing their optical axial figures to be easily observed. The guanidine salts are uniformly biaxial negative in

character and are most probably of monoclinic symmetry. Silver tungstomanganate forms rectangular prisms, which extinguish parallel to their principal length. There are indications that several of the other salts prepared are of cubic symmetry, including barium tungstomanganate and potassium and cæsium tungstoaluminates, but owing to the tendency to efflorescence of the barium and potassium salts, especially when crushed, observation is difficult. Crushed crystal fragments were used in all cases except for the guanidine salts, which were of convenient size for microscopic examination as obtained directly from their mother-liquors. The refractivity of these heteropoly-salts is very high; only with ammonium tungstoaluminate was the value below 1·7. The measurement thus required media of high refractive index, a saturated solution of the heavy-metal iodides (Sb, As, Sn, Bi) in methylene iodide being used for this purpose, dilution with more solvent being made as required.

Experimental.

The starting material for the preparation of the acids was a solution of sodium paratungstate, obtained by adding 194·4 ml. of N-nitric acid to a solution of 56·12 g. of sodium tungstate dihydrate in 400 ml. of water.

Tungstoaluminic Acid.—To the boiling sodium paratungstate solution, mechanically stirred, was added, during 20—24 hours, a solution of 10 g. of hydrated aluminium nitrate in 500 ml. of water. Complete hydrolysis of the aluminium nitrate being assumed, this gives nitric acid 30% in excess of that required (60·8 ml. of N) to convert the para- into meta-tungstate (cf. preceding paper, p. 2364). The precipitate formed with each drop of aluminium nitrate solution redissolved at once, and practically no permanent precipitate remained at the end of the saturation. The pH of the cold solution was below 4.

Tungstochromic Acid.—Under similar conditions, 8·1 g. of chromium nitrate nonahydrate in 500 ml of water gave rise to a pale green precipitate of a sodium chromium tungstate from an early stage; this partly redissolved at first but became permanent in the later stages. An average sample of this substance had the empirical formula $2Na_2O,Cr_2O_3,9WO_3,33H_2O$, and so was rather more basic than paratungstate. The pH of the cold solution was above 5, showing the presence of unchanged paratungstate. To remove this, 50 ml. of 4N-nitric acid were slowly added to the hot solution, the final pH being below 4. In the hope that chromium would enter the paratungstate nucleus more readily when present in anionic form, $K_4Cr(CN)_6$ and K_3CrF_6 were used instead of chromium nitrate, but hydrolysis of these salts was very incomplete, and their use was less satisfactory.

Tungstomanganic Acid.—Three methods of preparation were used, the third being the best. (1) To the boiling paratungstate solution were added 10 g. of fresh manganic hydroxide, prepared according to Meyer and Nerlich (*Z. anorg. Chem.*, 1921, **116**, 126). To the mechanically stirred suspension were added during 20—24 hours 67 ml. of N-nitric acid (10% excess) made up to 500 ml. The dark red colour of tervalent manganese deepened gradually, but in at least half the preparations hydrolysis took place quite suddenly in the later stages, precipitating the tervalent manganese already taken up, and leaving only a pale yellow solution, containing small amounts of a sodium manganous paratungstate. (2) Similarly, on addition of 8 g. of $K_3Mn(CN)_6$ simultaneously with 120 ml. of N-nitric acid (to react with the alkaline hydrolysis products), the $K_3Mn(CN)_6$ was seen to be immediately hydrolysed, and the hydroxide was rapidly taken up by the paratungstate. Appreciable amounts of H_3MnO_3 remained at the end of saturation. (3) To avoid the necessity for acidification during saturation, Friedheim and Keller's method (*loc. cit.*) for the preparation of molybdomanganates was tried, an intimate mixture of manganese sulphate tetrahydrate (7 g.) and potassium persulphate (9 g.) being added under the usual conditions to the paratungstate. The deep red colour of Mn(III) became more intense as saturation proceeded. There was little secondary precipitation of H_3MnO_3, and the final pH, owing to hydrolysis of the persulphate ion, was below 4, no acidification being necessary.

The Free Acids.—On completion of the saturations, the solutions were concentrated to about 200 ml., cooled, and kept at 6° for 20—24 hours to allow any unchanged paratungstate (not necessarily absent at pH values <4) to separate. The solutions, after filtration, were cooled in ice, mechanically stirred, and, after the addition of 300—400 ml. of dry ether, acidified slowly with 400 ml. of 6N-sulphuric acid. With tungstochromic acid emulsification was frequent and could not be avoided.

The mixture, on being transferred to a separating funnel, formed three layers, the lowest being the ether addition compound of the heteropoly-acid, colourless in the case of tungstoaluminic acid pale green with tungstochromic acid, and an intense dark red with tungstomanganic acid. These compounds were freed from entrained mother-liquor by dropping them through three successive portions of dry ether. They were finally run into water, and the ether was removed by an air current. The first two acids were finally isolated in solid form by evaporation to dryness, baking at 120—130°, extraction of the residue with water, and concentration *in vacuo* over sulphuric acid, as for tungstoferric acid. Tungstomanganic acid was too unstable to withstand this treatment, but its aqueous solution is comparatively stable and gives the corresponding salts without difficulty.

11-*Tungstoaluminic acid* is a colourless solid, very soluble in water, obtained only as crystal aggregates; it shows no definite break in the temperature–dehydration curve (Found: Al_2O_3, 1·66; WO_3, 84·70; H_2O, 14·31. $Al_2O_3,22WO_3,49H_2O$ requires Al_2O_3, 1·67; WO_3, 83·83; H_2O, 14·34%). Its apparent basicity was 10, as found by potentiometric titration with sodium hydroxide.*

* This acid can be represented as $H_{10}[Al_2W_{20}O_{72}].44H_2O$, and the other acids and their salts can be formulated as if containing a similar complex ion.

Ammonium 11-*tungstoaluminate*, prepared from aqueous solutions of the free acid by saturation with ammonium nitrate, formed perfectly transparent colourless octahedra, readily soluble in water [Found: $(NH_4)_2O$, 3·12; Al_2O_3, 1·43; WO_3, 84·07; H_2O, 10·43. $4(NH_4)_2O,Al_2O_3,22WO_3,36H_2O$ requires $(NH_4)_2O$, 3·43; Al_2O_3, 1·68; WO_3, 84·20; H_2O, 10·69%]; d 4·848; n 1·4599; pH of an approx. 0·002M-solution, 3·50. The crystals were stable in air, but became opaque on long exposure. From the original nitrate-containing mother-liquor the salt separates as rectangular prisms, recrystallising from water as octahedra.

Guanidine 11-*tungstoaluminate* was prepared by addition of guanidine hydrochloride solution to a solution of the free acid. It separated as a microcrystalline solid, giving, on recrystallisation from water, colourless leaflets or small rectangular prisms [Found: $(CN_3H_6)_2O$, 10·37; Al_2O_3, 1·69; WO_3, 84·78; H_2O, 3·16. $5(CN_3H_6)_2O,Al_2O_3,22WO_3,11H_2O$ requires $(CN_3H_6)_2O$, 11·00; Al_2O_3, 1·67; WO_3, 83·79; H_2O, 3·55%]; d 4·145. It was sparingly soluble in water; pH of approx. 0·002M-solution, 4·72. Crystals of this salt are biaxial negative and of small optic axial angle. The highest refractive index observed exceeds 1·78; the lowest is 1·768.

Potassium 11-tungstoaluminate, prepared from concentrated aqueous solutions of potassium nitrate and the free acid, formed large colourless octahedra, d 5·45, fairly soluble in water, but relatively easily hydrolysed when its solution is heated. The crystals are efflorescent, rapidly breaking down to a white microcrystalline powder on exposure to air. The pH of an approx. 0·002M-solution was 4·72. A complete analysis was not obtained, but Al_2O_3 : WO_3 was determined as *ca.* 1 : 22.

The barium and the cæsium salt are less well defined. The former is very soluble in water, separating from concentrated solutions as a white microcrystalline powder; the latter crystallises as colourless opaque prisms, sparingly soluble in water. Solutions of both salts are readily hydrolysed on heating.

11-Tungstochromic(III) acid was a pale green solid, obtained only as crystal aggregates from concentrated aqueous solutions. It was very soluble in water. No satisfactory analysis has been obtained for this acid, though it forms well-defined salts.

Ammonium 11-*tungstochromate*(III), prepared from concentrated aqueous solutions of ammonium nitrate or chloride and the free acid, exists as at least two different stable hydrates. The lower hydrate forms large transparent violet octahedra, perfectly isotropic. The higher hydrate forms large green octahedra or rectangular prisms. These are uniaxial positive, and probably of tetragonal symmetry. The green hydrate has refractive indices $\omega = 1·775$, $\varepsilon = 1·736$; d 4·619; and the pH of a 0·002M-solution is 2·83. Both hydrates are very soluble in water and are fairly stable in air [Found: $(NH_4)_2O$, 3·07; Cr_2O_3, 2·44; WO_3, 82·10; H_2O, 12·39. Green $4(NH_4)_2O,Cr_2O_3,22WO_3,43H_2O$ requires $(NH_4)_2O$, 3·33; Cr_2O_3, 2·44; WO_3, 81·81; H_2O, 12·41%].

Barium 11-*tungstochromate*(III), prepared from concentrated aqueous solutions of the free acid and barium chloride, or by direct neutralisation of the free acid with barium carbonate, forms large pale green transparent octahedra, rapidly efflorescent, giving a pale green microcrystalline powder (Found: BaO, 12·01; Cr_2O_3, 2·21; WO_3, 74·98; H_2O, 11·36. $5BaO,Cr_2O_3,22WO_3,43H_2O$ requires BaO, 11·28; Cr_2O_3, 2·24; WO_3, 75·08; H_2O, 11·39%); d 4·519; pH of 0·002M-solution, 2·95.

Guanidine 11-*tungstochromate*(III) separates as a pale green microcrystalline powder when aqueous solutions of guanidine hydrochloride and the free acid are mixed. Recrystallisation from water, in which it is sparingly soluble, gives small pale green leaflets or rectangular prisms [Found: $(CN_3H_6)_2O$, 11·39; Cr_2O_3, 2·47; WO_3, 83·24; H_2O, 2·61. $5(CN_3H_6)_2O,Cr_2O_3,22WO_3,9H_2O$ requires $(CN_3H_6)_2O$, 11·01; Cr_2O_3, 2·50; WO_3, 83·83; H_2O, 2·66%]. All three refractive indices are greater than 1·7; small optic axial angle; d 4·284; pH of 0·002M-solution, 2·54.

Potassium 11-tungstochromate(III) was prepared from concentrated aqueous solutions of potassium nitrate or chloride and the free acid. It forms large pale green transparent octahedra, d 4·976, rapidly efflorescing to a microcrystalline powder. Its aqueous solutions are readily hydrolysed; pH of approx. 0·002M-solution, 2·88. No complete analysis was obtained but Cr_2O_3 : WO_3 was determined as about 1 : 22.

11-*Tungstomanganic*(III) *Acid.*—This acid was obtained only in admixture with metatungstic acid, but its aqueous solution was stable and was used for the preparation of salts. There is no reduction on exposure to daylight.

Ammonium salt. Prepared from concentrated solutions of ammonium nitrate and the free acid, chloride ions being excluded because of their reducing properties, this *salt* forms large transparent deep red (almost black) octahedra [Found: $(NH_4)_2O$, 3·44; Mn_2O_3, 2·44; WO_3, 80·21; H_2O, 13·76. $4(NH_4)_2O,Mn_2O_3,22WO_3,49H_2O$ requires $(NH_4)_2O$, 3·27; Mn_2O_3, 2·48; WO_3, 80·35; H_2O, 13·89%], d 3·844, very soluble in water (pH of 0·002M-solution, 5·02), and becoming opaque on exposure to the air. Dehydration over phosphoric oxide gives isotropic crystals, n 1·798. There is also a higher hydrate which is anisotropic, probably tetragonal, and of lower refractive index.

Barium salt. Prepared by direct neutralisation of aqueous solutions of the free acid with barium carbonate, this *salt* forms large deep red transparent octahedra (Found: BaO, 12·64; Mn_2O_3, 2·47; WO_3, 79·94; H_2O, 5·63. $5BaO,Mn_2O_3,22WO_3,20H_2O$ requires BaO, 12·00; Mn_2O_3, 2·47; WO_3, 79·89; H_2O, 5·63%), fairly stable in air. It is isotropic; d 4·176; $n > 1·7$; pH of 0·002M-solution, 4·26.

Guanidine salt. This *salt* was prepared by mixing aqueous solutions of guanidine hydrochloride and the free acid. It is sparingly soluble, recrystallising from water as reddish-brown rectangular prisms, d 4·322 [Found: $(CN_3H_6)_2O$, 11·73; Mn_2O_3, 2·51; WO_3, 80·87; H_2O, 4·90. $5(CN_3H_6)_2O,Mn_2O_3,22WO_3,17H_2O$ requires $(CN_3H_6)_2O$, 10·74; Mn_2O_3, 2·53; WO_3, 81·81; H_2O, 4·90%]; pH of approx. 0·002M-solution, 4·49. Crystals of this salt are biaxial negative, and of small optical axial angle; the highest refractive index observed, γ, was 1·762, the lowest, α, being 1·728.

Silver salt. This was most probably of tetragonal symmetry; $n > 1{\cdot}7$; d 5·828; pH of 0·002*M*-solution, 2·44. The ratio $Mn_2O_3 : WO_3$ was determined as approx. 1 : 22.

Potassium salt. Prepared from concentrated aqueous solutions of potassium nitrate and the free acid, this salt forms large, transparent, deep red octahedra, d 5·094, readily efflorescing to give a reddish-brown microcrystalline powder. Aqueous solutions hydrolysed extensively on boiling; pH of 0·002*M*-solution, 4·47; $n > 1{\cdot}7$. The ratio $Mn_2O_3 : WO_3$ was found to be approx. 1 : 22.

The more soluble salts separate very slowly from their mother-liquors, in some cases only after several weeks at 6°.

Refractive-index Measurements.—A suitable medium was obtained by dissolving 20 g. of iodoform, 10 g. of sulphur, 8 g. of AsI_3, 5 g. of BiI_3, 5 g. of SnI_4, and 4 g. each of As_2S_3 and Sb_2S_3 in 50 g. of methylene iodide, and filtering. This solution was diluted with methylene iodide as required. As the refractive indices to be measured, with the exception of that of ammonium 11-tungstoaluminate, were outside the range of the Abbé refractometer, they were measured indirectly by dilution of the liquid with benzene or carbon tetrachloride, the mixture rule being used to calculate the index required. These values were checked by direct measurement, using a cell made from a microscope slide with a 0·5″ diameter hole cut in it, the base being a cover-slip cemented to the lower side. This gave a depth of liquid within the working distance of the microscope high-power objective.

Analysis.—Barium was determined as sulphate by double decomposition with dilute sulphuric acid, the anions of the free acids being sufficiently stable to permit this. Aluminium was determined by precipitation as hydroxide after removal of tungsten as cinchonine tungstate, both being ignited to the respective oxides. Chromium was determined by oxidation to chromate in alkaline solution, reduction with excess of ferrous sulphate, and back-titration. Manganese was precipitated as oxide with hydrogen peroxide in alkaline solution, converted into sulphate and weighed as such. Reduction of the tungstomanganates in hydrochloric–hydrobromic acid solution, followed by distillation of the bromine into excess of potassium iodide and titration of the iodine set free, established the tervalent state of the manganese and gave a confirmatory value for the metal. Ammonia was determined by distillation into standard acid, and guanidine by the micro-Dumas method (J.C.). Water was determined by dehydration at progressively rising temperatures, finally by ignition. No breaks in the temperature–dehydration curves were obtained corresponding to lower hydrates, decomposition usually beginning above 160°.

The authors thank Dr. T. H. Goodwin for advice and assistance in the microscopical measurements and Mr. James Cameron for micro-nitrogen determinations. One of them (J. L. T. W.) is also indebted to the Department of Scientific and Industrial Research for a maintenance grant covering part of the period of this work.

THE UNIVERSITY, GLASGOW, W.2. [*Received, May 18th*, 1950.]

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486. *Chemistry of New Zealand* Melicope *Species. Part IV.* Constituents of the Bark of* Melicope simplex.

By LINDSAY H. BRIGGS and R. H. LOCKER.

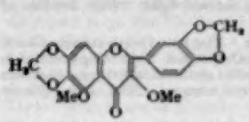
The dimethylchromens, evodionol and *allo*evodionol 7-methyl ether, the flavonols, meliternatin and ternatin, and two new flavonols, melisimplexin, $C_{20}H_{18}O_8$, and melisimplin, $C_{19}H_{16}O_8$, have been isolated from the bark of *Melicope simplex*. Degradative experiments show that the last two compounds are 3 : 5 : 6 : 7-tetramethoxy-3′ : 4′-methylenedioxyflavone and 5-hydroxy-3 : 6 : 7-trimethoxy-3′ : 4′-methylenedioxyflavone respectively.

Melicope simplex (genus *Melicope*, order *Rutaceae*, Maori name "Poataniwha") is a small tree 3—12 feet high, endemic to, and distributed through, both Islands of New Zealand. As with *Melicope ternata*, the inner bark is yellow, aromatic, and bitter.

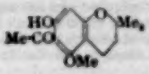
The resin, which separated during the extraction of the dried bark with light petroleum, was separated by fractional crystallisation into meliternatin, whose constitution has now been revised from that described in Part I (*J.*, 1949, 2157) to (I) (forthcoming communication) and two new flavonols, $C_{19}H_{16}O_8$ and $C_{20}H_{18}O_8$, for which the names melisimplin and melisimplexin respectively are proposed. The residual light-petroleum extract afforded (*a*) evodionol (II), a dimethylchromen derivative occurring in *Evodia littoralis* (Lahey and Jones, *Univ. Queensland Papers, Dept. Chem.*, 1939, **1**, No. 13; cf. Lahey, *ibid.*, 1940, **1**, No. 17; 1942, **1**, Nos. 20, 21), and (*b*) a further dimethylchromen derivative, *allo*evodionyl 7-methyl ether (III), first isolated by Jones and Wright (*Univ. Queensland Papers, Dept. Chem.*, 1946, **1**, No. 27) from the essential oil of a physiological form of *E. elleryana* and later by Sutherland (*ibid.*, 1949, **1**, No. 35) from the essential oil of *Medicosma cunninghamii*.

* Parts I—III of this series were published under the title "Flavonols from the Bark of *Melicope Ternata*."

In a separate experiment, the bark was extracted with acetone; and the extract afforded a minute amount of ternatin (IV) (cf. Parts I and III, *J.*, 1950, 864).



(I.)



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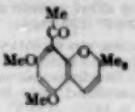

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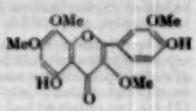


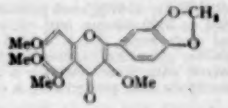
(IV.)

Melisimplexin, $C_{20}H_{18}O_8$.—Melisimplexin contains four methoxyl groups and gives a positive methylenedioxy-test. Reduction with magnesium in acid solution or sodium amalgam followed by acidification gave orange-red colours, indicative of a flavone with a methoxyl group at $C_{(3)}$. Its insolubility in alkalis, its negative ferric chloride reaction, and its solubility in concentrated hydrochloric acid with an intense yellow colour show that melisimplexin is a fully alkylated flavonol. It is therefore a tetramethoxymethylenedioxyflavone isomeric with meliternin, which it resembles very closely.

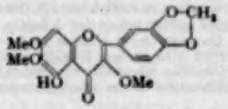
Hydrolysis with alcoholic potassium hydroxide gave quercetagetol tetramethyl ether and piperonylic acid. Melisimplexin must therefore be 3 : 5 : 6 : 7-tetramethoxy-3′ : 4′-methylenedioxyflavone (V), a derivative of quercetagetin.

Melisimplin, $C_{19}H_{16}O_8$.—Melisimplin contains three methoxyl groups and gives a positive test for the methylenedioxy-group. Reduction under the acid and the alkaline conditions previously mentioned indicated a flavonol methylated on $C_{(3)}$. Although insoluble in alkalis and concentrated hydrochloric acid it gave a green colour with ferric chloride characteristic of a 5-hydroxyflavonol with the remaining phenolic groups methylated (details of these observations will be submitted later). The presence of one free hydroxyl group was confirmed by the preparation of the monoacetate, $C_{21}H_{18}O_9$. Melisimplin must therefore be a 5-hydroxytrimethoxymethylenedioxyflavone. Methylation yielded melisimplexin, so that melisimplin must be 5-hydroxy-3 : 6 : 7-trimethoxy-3′ : 4′-methylenedioxyflavone (VI). The constitution of both melisimplexin and melisimplin has been confirmed by synthesis (succeeding paper).

For the small quantities of compounds isolated in these investigations we have found it expedient at times to purify the compounds as their acetyl derivatives, best prepared by acetic anhydride and a drop of 60% perchloric acid at room temperature (cf. Conant and Braunann,



(V.)



(VI.)

J. Amer. Chem. Soc., 1928, **50**, 2305). The flavonols do not dissolve in the acetic anhydride but do so immediately on the addition of the catalyst with the evolution of heat and production of a red colour. In some cases yellow crystals separate which decompose in water to give the colourless acetate. It appears that the initial product is the perchlorate of the acetate. Complete and immediate hydrolysis occurred when the flavonol acetates were dissolved in cold concentrated sulphuric acid. Dilution of the acid deposited the pure flavonol. Equal success has been attained in the hydroxyanthraquinone series.

Experimental.

(M. p.s are corr.)

Isolation of Constituents.—The bark was collected in August from mature trees of *Melicope simplex* growing in the northern Waitakere Ranges. The dark outer layer was scraped off and the yellow inner bark dried in air and finely powdered.

In a pilot experiment the bark (66 g.) was extracted with light petroleum (b. p. 50—60°) for 3 hours in a Soxhlet extractor. The extract was cooled and the clear yellow solution decanted from the residual brown resin which was dissolved in acetone. On concentration and cooling of the filtered acetone solution, an amorphous material separated which crystallised from alcohol in needles, m. p. 185—186° (76 mg.). Further recrystallisation from ethyl acetate gave two crops, (i) cream-coloured needles, m. p. 223—225° (20 mg.), of *melisimplin* (see below) and (ii) an amorphous solid, m. p. 197—197·5° (23 mg.). The latter, on crystallision twice from alcohol, formed small colourless needles, m. p. and mixed m. p. with meliternatin, 198—199°.

The main quantity of bark (420 g.) was extracted with light petroleum (b. p. 50—60°) for 24 hours. After cooling, the liquid was decanted and the solid residue dissolved in acetone. The filtered acetone solution was concentrated to *ca.* 100 c.c. and set aside. The crystalline material which separated, after repeated crystallisation from ethyl acetate and finally from acetone, formed light yellow needles of melisimplin, m. p. 233·5—234·5° (236 mg.).

The original acetone solution was further concentrated and set aside. The pale cream-coloured solid separating was purified by being dissolved in the first ethyl acetate mother-liquor from the purification of melisimplin and set aside. Slender cream-coloured needles were separated mechanically from colourless amorphous material and crystallised twice from alcohol and finally from acetone. The *melisimplexin* (37 mg.) so obtained had m. p. 182·5—183·5°.

The amorphous material crystallised from alcohol in small colourless needles, m. p. 186—189° (252 mg.). The m. p. was not depressed by meliternatin but attempts to raise it by further recrystallisation were unsuccessful. Better, but not complete, separation was achieved by chromatography. The material was absorbed on freshly activated alumina from a chloroform solution, developed with dry chloroform, and eluted in eight 30-c.c. fractions with acetone. The material from the second fraction gave on evaporation a colourless crystalline residue (220 mg.), m. p. 161—165°, raised to 183·5—184·5°, that of melisimplexin, on recrystallisation from alcohol and twice from acetone (total yield of melisimplexin, *ca.* 70 mg.).

The residues from the third—sixth fractions were combined and after crystallisation from alcohol and dioxan–water formed colourless needles of meliternatin, m. p. 198—198·5°.

The light-petroleum solution from the original extraction was shaken successively with saturated sodium hydrogen carbonate, sodium carbonate, and 10% sodium hydroxide solution. The first two fractions were only slightly coloured and were not investigated. The sodium hydroxide extracts, however, were bright yellow and on acidification yielded evodionol as a dark yellow solid, crystallising from alcohol in rhombic prisms, m. p. 85—86·5° (287 mg.).

The light-petroleum fraction was then shaken with 5% hydrochloric acid. Alkaloids were not present in appreciable quantity, as shown by the very slight precipitates when the acid extracts were treated with Mayer's and Dragendorff's reagents.

Finally, the light petroleum extract was concentrated and set aside. Yellow crystals separated with resinous material but, after repeated crystallisation from alcohol, colourless rhombic plates of *allo*evodionyl 7-methyl ether, m. p. 105·5—106° (534 mg.), were obtained.

In a further experiment, a sample of bark was extracted with acetone and the solid extract dissolved in chloroform. This solution was washed successively with sodium hydrogen carbonate, carbonate, and hydroxide solutions. The material obtained by acidifying the last extract crystallised in slender yellow needles (*ca.* 3 mg.), m. p. and mixed m. p. with ternatin, 210—212°.

Melisimplexin.—Melisimplexin crystallises from acetone in colourless flattened needles, m. p. 183·5—184·5°, with an unusually high solubility in hot alcohol (Found: C, 62·0; H, 4·8; OMe, 31·4. $C_{20}H_{14}O_8$ requires C, 62·2; H, 4·7; 4OMe, 32·1%). It gave a green colour within 10 minutes in the methylenedioxy-test with concentrated sulphuric acid and gallic acid.

Hydrolysis. A solution of melisimplexin (99 mg.) in alcohol (2 c.c. of 80%) and potassium hydroxide (200 mg.) was heated under reflux for 5 hours, concentrated to half volume, and diluted with water (2 c.c.). Most of the remaining alcohol was boiled off and more water (3 c.c.) added. The filtered solution was saturated with carbon dioxide, precipitating slender colourless needles (fraction I). After removal of the crystalline material, the residue was extracted with ether, yielding a greasy residue (fraction II). Acidification of the aqueous layer with hydrochloric acid precipitated a colourless solid (fraction III).

Fraction I (38 mg.) was a potassium salt. When acidified with dilute hydrochloric acid it yielded, through extraction by ether, a colourless solid which, after 3 crystallisations from water, formed needles, m. p. and mixed m. p. with a specimen of quercetagetol tetramethyl ether prepared synthetically (succeeding paper), 71°. Also in agreement with this identification were its insolubility in sodium carbonate solution, its ready solubility in 10% sodium hydroxide solution, and its brown colour with ferric chloride. Fraction II afforded a further 11 mg. of the same compound by similar treatment.

Fraction III (32 mg.) recrystallised from alcohol in colourless prisms, m. p. and mixed m. p. with piperonylic acid, 233°.

Melisimplin.—Melisimplin crystallises from ethyl acetate or acetone in light yellow needles, m. p. 234—235° (Found: C, 60·8; H, 4·5; OMe, 21·8, 23·0. $C_{12}H_{14}O_8$ requires C, 61·3; H, 4·3; 3OMe, 25·0%). It forms a bright yellow solution with concentrated sulphuric acid and with gallic acid this changes to a clear green within ½ hour. A pink colour is produced on reduction with magnesium and hydrochloric acid or with sodium amalgam followed by acidification.

Melisimplin (25 mg.) was treated with acetic anhydride (0·5 c.c.) and 60% perchloric acid (1 drop) in the cold. Yellow crystals formed when the orange solution was stirred. After addition of water, however, a colourless *acetate* formed which crystallised from alcohol in colourless needles, m. p. 201·5—202° (Found: C, 60·7; H, 4·4. $C_{21}H_{18}O_9$ requires C, 60·9; H, 4·3%).

Methylation of melisimplin to melisimplexin. Melisimplin (50 mg.), in dry acetone (8 c.c.), was refluxed for 5 hours with methyl sulphate (0·04 c.c., 3 mols.) and anhydrous potassium carbonate (0·5 g.). The acetone portion and washings of the solid material, on concentration, afforded colourless needles which, after recrystallisation from alcohol, had m. p. and mixed m. p. with melisimplexin, 181·5—182·5°.

Dealkylation of melisimplin. Melisimplin (40 mg.) was heated for 1 hour at 140° with hydriodic acid (3 c.c.; *d* 1·7) in an atmosphere of carbon dioxide. The brown solid (34 mg.) formed when the mixture

was poured into water was acetylated with acetic anhydride and a trace of 60% perchloric acid, and the process repeated to ensure complete acetylation. The product could not be crystallised but sublimed at 220°/0·01 mm. The sublimate, after two crystallisations from alcohol, formed colourless needles with m. p. 201—202°, still lower than that of quercetagetin hexa-acetate (m. p. 212—213°; cf. Part I) but the mixed m. p. was 204·5—205°. There was insufficient material for further purification.

Evodionol.—This compound crystallised from alcohol in yellow prisms, m. p. and mixed m. p. with evodionol, 86—86·5° [Found: C, 67·9; H, 6·5%; *M* (ebullioscopic in benzene), 233. Calc. for $C_{14}H_{14}O_5$: C, 67·8; H, 6·4%; *M*, 248]. It dissolved in sodium hydroxide solution and concentrated sulphuric acid yielding faintly and intensely yellow solutions respectively, and the ferric chloride reaction was green. These reactions are all given by the authentic compound.

Confirmation was provided by the preparation of the methyl ethers as described above for melisimplin. The methyl ether crystallised from alcohol in colourless rhombic prisms, m. p. 79·5—80°, identical, by mixed m. p., with a sample of the same m. p. prepared from authentic evodionol.

allo*Evodionyl* 7-*Methyl Ether.*—This constituent crystallised from alcohol in rhombic plates, m. p. and mixed m. p. with *allo*evodionyl 7-methyl ether, 105·5—106° (Found: C, 69·0; H, 7·1. Calc. for $C_{15}H_{16}O_5$: C, 68·7; H, 6·9%). It was slightly soluble in concentrated hydrochloric acid and freely soluble in concentrated sulphuric acid with an intensely yellow colour. The benzylidene derivative, prepared according to Sutherland (*loc. cit.*), crystallised from methyl alcohol in yellow prisms, m. p. and mixed m. p. with benzylidene *allo*evodionyl 7-methyl ether, 165·5—166·5°.

The analyses are by Drs. Weiler and Strauss, Oxford. We are indebted to the Chemical Society, the Royal Society of New Zealand, the Australian and New Zealand Association for the Advancement of Science, and the Research Grants Committee of the University of New Zealand for grants and for a Research Scholarship to one of us (R. H. L.), and to Messrs. M. D. Sutherland and S. E. Wright for samples of evodionol and *allo*evodionyl methyl ether.

AUCKLAND UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, May 30th*, 1950.]

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487. *Chemistry of New Zealand* Melicope *Species. Part V. A Synthesis of 6-Hydroxy-3 : 5 : 7-trimethoxy-3′ : 4′-methylenedioxyflavone, Melisimplexin, and Melisimplin.*

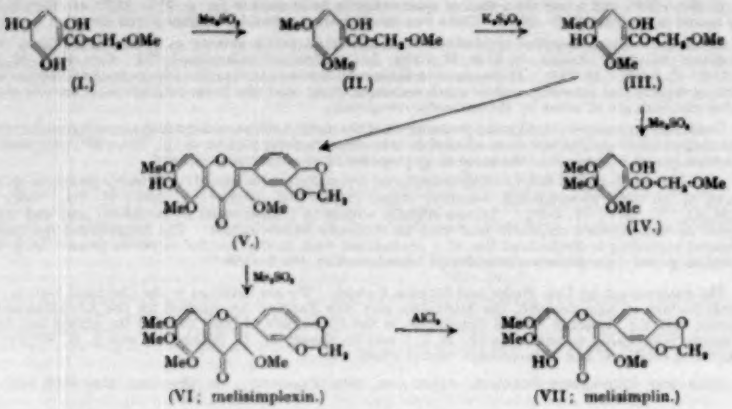
By LINDSAY H. BRIGGS and R. H. LOCKER.

The above compounds have been synthesised by an application of the method of Row and Seshadri (*Proc. Indian Acad. Sci.*, 1946, **23**, *B*, 23) for the synthesis of 5 : 6 : 7-hydroxyflavonols.

SESHADRI and his co-workers (cf. Balakrishna, Seshadri, and Viswanath, *Proc. Indian Acad. Sci.*, 1949, **30**, A, 120, and earlier papers) have introduced methods for the nuclear oxidation of flavones leading to 5 : 8-di- and 5 : 7 : 8-tri-hydroxy-derivatives. 5 : 6 : 7-Trihydroxy-derivatives cannot be thus prepared but Row and Seshadri (*ibid.*, 1946, **23**, *B*, 23) were successful by employing nuclear oxidation at the acetophenone stage before condensation to the flavone. By an application of the last method, 6-hydroxy-3 : 5 : 7-trimethoxy-3′ : 4′-methylenedioxyflavone, melisimplexin, and melisimplin, all 5 : 6 : 7-derivatives, have been synthesised according to the scheme shown on the next page.

Partial methylation of 2 : 4 : 6-trihydroxy-ω-methoxyacetophenone (I) with 2 moles of methyl sulphate afforded the 2 : 4-dimethyl ether (II), oxidised by potassium persulphate to 3 : 6-dihydroxy-2 : 4 : ω-trimethoxyacetophenone (III). Partial methylation of the last named compound yielded quercetagetol tetramethyl ether (IV) required for comparison with one of the hydrolytic products of melisimplexin (cf. Part IV, preceding paper). Condensation of (III) with piperonylic anhydride and potassium piperonylate followed by treatment with alcoholic potassium hydroxide afforded 6-hydroxy-3 : 5 : 7-trimethoxy-3′ : 4′-methylenedioxyflavone (V). Methylation gave melisimplexin (VI), identified by mixed melting point and its ultra-violet absorption spectrum. Partial demethylation of melisimplexin with aluminium chloride in boiling ethereal solution afforded melisimplin (VII). Methoxyl groups at $C_{(3)}$ are demethylated by aluminium chloride only at 100°, and not at room temperature (cf. Shah, Virkar, and Venkataraman, *J. Indian Chem. Soc.*, 1942, **19**, 135), whereas methoxyl groups at $C_{(3)}$ are demethylated under the above conditions (cf. Baker, *J.*, 1939, 961; Baker and Wilson, *J.*, 1940, 1370). This agrees with the converse properties of 3 : 5-dihydroxyflavones where the 3-hydroxyl is more readily methylated than the 5-hydroxyl group, and is in harmony with the naturally occurring partly methylated 3 : 5-dihydroxyflavones. No naturally occurring 3 : 5-dihydroxyflavone exists which is methylated at $C_{(3)}$ but not at $C_{(5)}$, whereas there are numerous examples of the inverse case. For these and other reasons (cf. Part IV) the free hydroxyl group of

melisimplin is placed at C_{6_2}, and the constitutions of melisimplexin and melisimplin based on degradative experiments (Part IV) are thus confirmed.



Experimental.

(M. p.s are corr.)

6-Hydroxy-3 : 5 : 7-trimethoxy-3' : 4'-methylenedioxyflavone.—2 : 4 : 6-Trihydroxy-ω-methoxyacetophenone (Slater and Stephen, *J.*, 1920, 312) was partly methylated, and 2-hydroxy-4 : 6 : ω-trimethoxyacetophenone obtained as thin colourless plates, m. p. 98—100°, from alcohol–water (1 : 2). Row and Seshadri (*loc. cit.*) record colourless prisms, m. p. 103—104°. Persulphate oxidation of the product afforded 3 : 6-dihydroxy-2 : 4 : ω-trimethoxyacetophenone, crystallising from water in bright yellow, slender, flat needles, m. p. 139·5—141·5°. Addition of benzoyl peroxide did not improve the yield above that obtained by Row and Seshadri (*loc. cit.*), who obtained rhombohedral plates, m. p. 135—136°. Methylation of the last named product according to Row and Seshadri yielded quercetagetol tetramethyl ether, m. p. 71°, crystallising from water in colourless needles, undepressed in m. p. by a product of the same m. p. obtained by hydrolysis of melisimplexin (Part IV, *loc. cit.*). Row and Seshadri (*loc. cit.*) record long, rectangular plates, m. p. 77—78°.

3 : 6-Dihydroxy-2 : 4 : ω-trimethoxyacetophenone (680 mg., 1 mol.), piperonylic anhydride (2·2 g., 2·5 mols.; Rao and Seshadri, *Proc. Indian Acad. Sci.*, 1946, **23**, 148) and potassium piperonylate (920 mg., 1·5 mols.) were powdered together and heated at 170—175°/300 mm. for 2 hours. The fawn-coloured melt was powdered and boiled for a short time with alcohol (60 c.c.) and water (4 c.c.) containing potassium hydroxide (6 g.). The bulk of the alcohol was distilled off under reduced pressure and the volume made up to 50 c.c. with water. When carbon dioxide was bubbled into the solution, crystalline *6-hydroxy-3 : 5 : 7-trimethoxy-3' : 4'-methylenedioxyflavone* (440 mg.) separated, which, after 3 recrystallisations from alcohol, formed colourless, hexagonal plates, m. p. 244·5—246° (Found: C, 61·8; H, 4·6. $C_{19}H_{16}O_8$ requires C, 61·3; H, 4·3%). The flavonol is insoluble in sodium carbonate solution but soluble in sodium hydroxide solution forming a yellow solution from which the sodium salt soon separates as needles. It has a limited solubility in concentrated hydrochloric acid but dissolves freely in concentrated sulphuric acid with a bright yellow colour. Ferric chloride produces no colour, but acid or alkaline reduction gives strong red colours.

The *monoacetate*, prepared with acetic anhydride and perchloric acid, after crystallisation from alcohol and dioxan, formed colourless, rhombic plates, m. p. 246—247° (Found: C, 61·2; H, 4·4. $C_{21}H_{18}O_9$ requires C, 60·9; H, 4·3%).

Melisimplexin.—A solution of the foregoing flavonol (250 mg.) in dry acetone (10 c.c.) was heated under reflux with methyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.) for 4 hours. Concentration of the acetone portion and washings yielded colourless, flat needles (217 mg.), which, after recrystallisation from acetone, had m. p. 185—185·5°, undepressed by an authentic sample of melisimplexin. The ultra-violet absorption spectra of the natural and synthetic specimens also corresponded (forthcoming communication).

Melisimplin.—A solution of melisimplexin (150 mg.) and aluminium chloride (1 g.) in dry ether (4 c.c.) was heated under reflux for 10 hours. After the solution had been poured into water and the whole kept for several hours, the precipitate was boiled with glacial acetic acid (5 c.c.) and concentrated hydrochloric acid (2·5 c.c.) for 20 minutes. The yellow solid which formed on dilution, after successive crystallisation from ethyl acetate and acetone, formed yellow needles (75 mg.), m. p. and mixed m. p. with melisimplin, 235—236°. The acetate (cf. Part IV), after crystallisation successively from ethyl and

methyl alcohol, was obtained as colourless needles, m. p. 199·5—200·5°, undepressed by a sample of the natural derivative, m. p. 201·5—202°.

The analyses are by Drs. Weiler and Strauss, Oxford. We are indebted to the Chemical Society, the Royal Society of New Zealand, the Australian and New Zealand Association for the Advancement of Science, and the Research Grants Committee of the University of New Zealand for grants and a Research Scholarship to one of us (R. H. L.).

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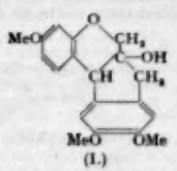
488. *Furano-compounds. Part XI. The Synthesis of α-Anhydro-O-trimethylbrazilone and Related Compounds.*

By P. C. JOHNSON and ALEXANDER ROBERTSON.

A series of 4′- and 3′-hydroxynaphtho(2′ : 1′-2 : 3)coumarones of the α-anhydrobrazilone type has been synthesised. 3-(3 : 4-Dimethoxyphenyl)-6-methoxycoumarone (VI; R = H) was prepared from 5-methoxy-2-veratroylphenoxyacetic acid (V; R = H), and its 2-formyl derivative (VI; R = CHO) was converted by the azlactone method into 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-acetic acid (VIII) which on cyclisation gave 4′-hydroxy-6 : 6′ : 7′-trimethoxynaphtho(2′ : 1′-2 : 3)coumarone (IX). 4′-Hydroxy-6 : 6′- and -6 : 7′-dimethoxynaphtho(2′ : 1′-2 : 3)coumarone were also synthesised by the same general route.

3-o-Carboxyphenyl-6-methoxycoumarone (XII; R = OH, R′ = H) was prepared from 2-o-carboxybenzoyl-5-methoxyphenoxyacetic acid (XI; R = R′ = H), and converted into the acetic acid (XIII; R = H) which on cyclisation gave 3′-hydroxy-6-methoxynaphtho(2′ : 1′-2 : 3)coumarone (XIV). By the same route α-anhydro-*O*-trimethylbrazilone (IV) was synthesised from brazilinic acid (XI; R = H, R′ = OMe).

By the oxidation of *O*-trimethylbrazilin (I) with chromic acid Gilbody and Perkin (*J.*, 1902, **81**, 1008; cf. *Proc. Chem. Soc.*, 1899, **15**, 27) obtained *O*-trimethylbrazilone which by loss of water under comparatively mild conditions gave α-anhydro-*O*-trimethylbrazilone. Subsequently Perkin and Robinson (*J.*, 1908, **93**, 498) formulated *O*-trimethylbrazilone as (III), a constitution which explains the majority of the remarkable reactions of this compound. These authors also suggested that the primary oxidation product of *O*-trimethylbrazilin was the diketone (II) which immediately undergoes an intramolecular aldol condensation giving (III), and from an examination of the properties and reactions of α-anhydro-*O*-trimethylbrazilone they concluded that it was a β-naphthol derivative (IV) (*loc. cit.*; *J.*, 1909, **95**, 381).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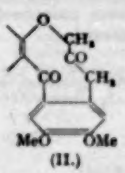
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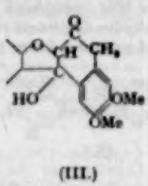
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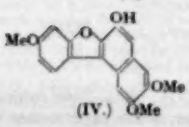
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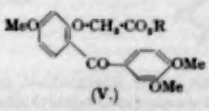
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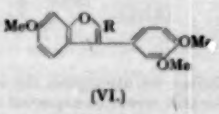
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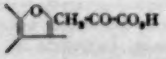
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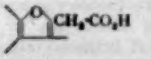
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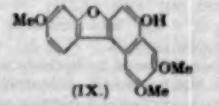

(IX.)

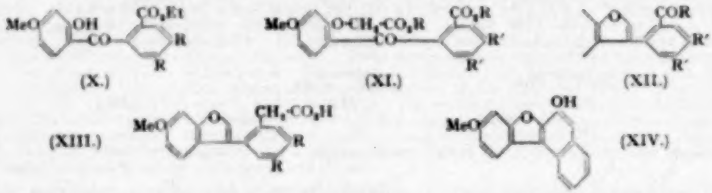
For the synthesis of α-anhydro-*O*-trimethylbrazilone (IV) there appeared to be two promising routes, *viz.*, the preparation and cyclisation (*a*) of the diazo-ketone (VI; R = $CO{\cdot}CHN_2$) according to the method of Cook and Schoental (*J.*, 1945, 288) and (*b*) of the acid (XIII; R = OMe) which from the established reactivity of the α-position of the coumarone residue

would be expected to give (IV) (Robertson *et al.*, Part VII, *J.*, **1948**, 2254; Part X, *J.*, **1949**, 2057). Naphtho(2′ : 1′-2 : 3)coumarone derivatives of the α-anhydrobrazilone type do not appear to have been synthesised and, before proceeding to the synthesis of (IV), exploratory experiments on the preparation of typical 3-phenylcoumarone-2-acetic acids and their conversion into α-naphthol derivatives analogous to (IV) were carried out.

Ethyl 5-methoxy-2-veratroylphenoxyacetate (V; R = Et) was prepared from 2-hydroxy-4 : 3′ : 4′-trimethoxybenzophenone and ethyl bromoacetate by the potassium carbonate–acetone method, and gave on hydrolysis the acid (V; R = H) which was cyclised with sodium acetate and hot acetic anhydride to 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone (VI; R = H). 3-(3 : 4-Dimethoxyphenyl)-2-formyl-6-methoxycoumarone (VI; R = CHO) was obtained from (VI; R = H) by Gattermann's method, and its orientation established by oxidation with potassium permanganate in acetone to 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-carboxylic acid (VI; R = CO_2H), identical with a specimen prepared by the hydrolysis of the ester (VI; R = CO_2Et) which was formed by the cyclisation of (V; R = Et) with alcoholic sodium ethoxide. Condensation of the aldehyde (VI; R = CHO) with hippuric acid in the usual manner gave the azlactone, and on hydrolysis this compound yielded 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-pyruvic acid (VII) which was oxidised with alkaline hydrogen peroxide, giving 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-acetic acid (VIII). Attempts to cyclise the acid (VIII) to 4′-hydroxy-6 : 6′ : 7′-trimethoxynaphtho(2′ : 1′-2 : 3)-coumarone (IX) by sulphuric acid or by an intramolecular Friedel–Crafts reaction on the acid chloride with aluminium chloride in nitrobenzene were unsuccessful but treatment with phosphoric oxide in boiling benzene gave the naphthol in small yield.

From the requisite benzophenones, 4′-hydroxy-6 : 7′- and -6 : 6′-dimethoxynaphtho(2′ : 1′-2 : 3)coumarone were prepared by the same general method; however, in the synthesis of the last-mentioned compound hydrolysis of the azlactone obtained from 2-formyl-6-methoxy-3-*m*-methoxyphenylcoumarone gave a poor yield of the pyruvic acid, and the required acetic acid was prepared in quantity by way of its amide from 6-methoxy-3-*m*-methoxyphenylcoumarone-2-carboxylic acid, according to the procedure of Arndt and Eistert. The 4′-hydroxynaphtho-(2′ : 1′-2 : 3)coumarones resemble α-anhydro-*O*-trimethylbrazilone (IV) in readily forming azo-dyes with diazonium chlorides but can be readily distinguished from it by their failure to give the striking blue colour with warm alcoholic potassium hydroxide containing a little chloroform, characteristic of (IV) as well as of (XIV).

The well-crystallised diazo-ketone (VI; R = CO·CHN_2) was prepared from 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-carboxylic acid in the usual manner but our attempts to induce this compound to undergo the Cook–Schoental cyclisation (*loc. cit.*) and thus give α-anhydro-*O*-trimethylbrazilone were unsuccessful. The alternative route to the last-mentioned compound was therefore explored.



Before we attempted the synthesis of the intermediate acid (XIII; R = OMe) which on cyclisation would be expected to give α-anhydro-*O*-trimethylbrazilone, model experiments were carried out with (XIII; R = H). 2-*o*-Carboxybenzoyl-5-methoxyphenoxyacetic acid (XI; R = R′ = H) was prepared by the interaction of 2′-carbethoxy-2-hydroxy-4-methoxybenzophenone (X; R = H) with ethyl bromoacetate and potassium carbonate in boiling acetone, followed by hydrolysis of the resulting ester (XI; R = Et, R′ = H) and, on treatment with boiling acetic anhydride containing sodium acetate, this acid was converted into 3-*o*-carboxyphenyl-6-methoxycoumarone (XII; R = OH, R′ = H). With diazomethane the acid chloride of (XII; R = OH, R′ = H) gave the diazo-ketone (XII; R = CHN_2, R′ = H) from which the 2′-acetic acid (XIII; R = H) was prepared by way of the amide (Arndt–Eistert). On cyclisation with sulphuric acid (XIII; R = H) yielded 3′-hydroxy-6-methoxynaphtho(2′ : 1′-2 : 3)coumarone, the properties of which closely resemble those of α-anhydro-*O*-

trimethylbrazilone. Similarly, brazilinic acid has been prepared by a new route from 2′-carbethoxy-2-hydroxy-4 : 4′ : 5′-trimethoxybenzophenone (X; R = OMe) (cf. Perkin and Robinson, *loc. cit.*; Rây *et al.*, *J. Indian Chem. Soc.*, 1933, **10**, 617), and on treatment with boiling acetic anhydride and potassium acetate gave 3-(2′-carboxy-4′ : 5′-dimethoxyphenyl)-6-methoxycoumarone (XII; R = OH, R′ = OMe) from which the acetic acid (XIII; R = OMe) was prepared by way of the diazo-ketone (XII; R = CHN_2, R′ = OMe). When cyclised with sulphuric acid, the acid (XIII; R = OMe) furnished 3′-hydroxy-6 : 6′ : 7′-trimethoxynaphtho(2′ : 1′-2 : 3)coumarone, the properties and derivatives of which were identical with those of α-anhydro-*O*-trimethylbrazilone from natural sources.

Experimental.

2 : 4-*Dihydroxy*-3′ : 4′-*dimethoxybenzophenone*.—Attempts to prepare this compound by the condensation of veratronitrile and resorcinol by the method of Hoesch were unsuccessful. It was obtained by the following methods.

(a) An intimate mixture of resorcinol (2 g.), veratric acid (3 g.), and powdered zinc chloride (3 g.) was heated at 160° (oil-bath) for 7 minutes, cooled, and treated with hot water (50 ml.). Crystallisation of the orange residue from dilute alcohol gave 2 : 4-*dihydroxy*-3′ : 4′-*dimethoxybenzophenone* in pale yellow rhombic plates (1·1 g.), m. p. 177°, having a red-brown ferric reaction in alcohol (Found: C, 65·8; H, 5·0. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·1%). This ketone was readily soluble in acetone and almost insoluble in benzene.

(b) Aluminium chloride (16 g.) was added gradually to a mixture of resorcinol (9 g.), veratroyl chloride (16 g.), and nitrobenzene (120 ml.) during 30 minutes, and 3 days later the reaction mixture was poured on ice (100 g.) and hydrochloric acid (200 ml.). After the removal of the nitrobenzene with steam the residual solid was triturated with aqueous sodium hydrogen carbonate, washed with water and then with cold methanol (100 ml.) to remove tarry impurities, and crystallised from dilute methanol, giving 2 : 4-dihydroxy-3′ : 4′-dimethoxybenzophenone in pale yellow rhombic plates (13—14 g.), m. p. and mixed m. p. 177°.

Methylation of this ketone (10 g.) with methyl iodide (2·7 ml.) and potassium carbonate (15 g.) in boiling acetone (100 ml.) during 1½ hours gave 2-hydroxy-4 : 3′ : 4′-trimethoxybenzophenone which formed clusters of pale yellow needles (9·4 g.), m. p. 140°, from carbon tetrachloride, having a red-brown ferric reaction in alcohol (Found: C, 66·2; H, 5·8. Calc. for $C_{16}H_{16}O_5$: C, 66·7; H, 5·6%) (compare Appel *et al.*, *J.*, 1937, 738, and Rây *et al.*, *loc. cit.*). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in deep-red prisms, m. p. 231° (Found: N, 12·0. $C_{28}H_{28}O_9N_4$ requires N, 11·9%).

5-*Methoxy*-2-*veratroylphenoxyacetic Acid* (V; R = H).—A mixture of 2-hydroxy-4 : 3′ : 4′-trimethoxybenzophenone (25 g.), ethyl bromoacetate (16 ml.), potassium carbonate (70 g.), and acetone (300 ml.) was heated under reflux for 8 hours. On isolation the resulting *ethyl 5-methoxy-2-veratroylphenoxyacetate* (V; R = Et) crystallised from dilute alcohol in colourless needles (31 g.), m. p. 80°, having a negative ferric reaction (Found: C, 63·8; H, 5·9. $C_{22}H_{26}O_7$ requires C, 64·2; H, 5·9%). This compound was readily soluble in alcohol, methanol, benzene, or ethyl acetate and sparingly soluble in light petroleum.

A solution of this ester (32 g.) and potassium hydroxide (30 g.) in alcohol (150 ml.) containing water (100 ml.) was heated under reflux for ½ hour, the greater part of the alcohol was removed in a vacuum, the residue was diluted with water (500 ml.), and the resulting *acid* precipitated with dilute hydrochloric acid. Crystallised from ethyl acetate–light petroleum (b. p. 60—80°), this acid formed clusters of colourless needles (27 g.), m. p. 149°, readily soluble in alcohol, acetic acid, or ethyl acetate (Found: C, 62·3; H, 5·3. $C_{18}H_{18}O_7$ requires C, 62·4; H, 5·2%).

3-(3 : 4-*Dimethoxyphenyl*)-6-*methoxycoumarone* (VI; R = H).—A mixture of 5-methoxy-2-veratroylphenoxyacetic acid (6 g.), sodium acetate (12 g.), and acetic anhydride (60 ml.) was heated at 150—160° (oil-bath) for ½ hour and poured into water (600 ml.). Next day the solid was collected, well washed with aqueous sodium hydrogen carbonate, and crystallised from dilute acetic acid (charcoal), yielding 3-(3 : 4-*dimethoxyphenyl*)-6-*methoxycoumarone* in colourless plates (4·2 g.), m. p. 74°, which gave a bright red colour with concentrated sulphuric acid (Found: C, 71·4; H, 5·5. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). This compound is easily soluble in the usual organic solvents except light petroleum.

3-(3 : 4-*Dimethoxyphenyl*)-2-*formyl*-6-*methoxycoumarone* (VI; R = CHO).—A solution of 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone (5 g.) and hydrogen cyanide (7 ml.) in ether (150 ml.) containing zinc chloride (2 g.) was saturated with hydrogen chloride at 0° and next day the product, which had separated in orange-yellow needles, was washed with ether and hydrolysed with water (250 ml.) on the steam-bath for 25 minutes. On isolation from the cooled hydrolysate the resulting *aldehyde* formed pale yellow needles (5 g.), m. p. 158°, from alcohol (Found: C, 69·3; H, 5·1. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%). On being diluted with water the bright red solution of this compound in warm concentrated sulphuric acid became green and then bright blue. The 2 : 4-*dinitrophenylhydrazone* separated from nitrobenzene–alcohol in crimson needles, m. p. 260° after sintering at 255° (Found: N, 11·3. $C_{24}H_{20}O_8N_4$ requires N, 11·4%).

3-(3 : 4-*Dimethoxyphenyl*)-6-*methoxycoumarone*-2-*carboxylic Acid* (VI; R = CO_2H).—(*a*) A solution of ethyl 5-methoxy-2-veratroylphenoxyacetate (14·1 g.) and sodium ethoxide (from 1·15 g. of sodium) in absolute alcohol (90 ml.) was heated under reflux for 1 hour and then treated with water (800 ml.). Next day the resulting *ethyl* 3-(3 : 4-*dimethoxyphenyl*)-6-*methoxycoumarone*-2-*carboxylate* (VI; R = CO_2Et) was isolated and purified from dilute alcohol, forming elongated, pale yellow needles (5·8 g.), m. p. 134°,

having a bright red sulphuric acid reaction (Found: C, 67·2; H, 5·7. $C_{20}H_{20}O_6$ requires C, 67·5; H, 5·6%).

On being acidified with dilute hydrochloric acid the alkaline liquors left after the separation of the crude ester deposited a solid which, on crystallisation from acetic acid, gave 3-(3 : 4-*dimethoxyphenyl*)-6-*methoxycoumarone*-2-*carboxylic acid* in colourless prismatic needles (1·5 g.), m. p. 204° (decomp.) (Found: C, 65·9; H, 5·1. $C_{12}H_{14}O_6$ requires C, 65·9; H, 4·9%), identical with a specimen (6·5 g.) prepared by the hydrolysis of the foregoing ethyl ester (8 g.) with a boiling solution of potassium hydroxide (10 g.) in water (80 ml.) and alcohol (120 ml.) during ½ hour. This compound, which is soluble in alcohol, ethyl acetate, or acetone and almost insoluble in benzene, gave a red colour with cold sulphuric acid changing to deep violet in warm acid.

From the acetic acid liquors left from the purification of the crude 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-carboxylic acid mixture, 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone (1·8 g.) and 5-methoxy-2-veratroylphenoxyacetic acid (1·3 g.) were isolated and separated by fractional crystallisation from dilute acetic acid.

(*b*) A solution of potassium permanganate (1 g.) in water (20 ml.) at 50° was gradually added during ½ hour to 3-(3 : 4-dimethoxyphenyl)-2-formyl-6-methoxycoumarone (0·4 g.), dissolved in acetone (20 ml.), and 1 hour later the mixture was cooled, cleared with sulphur dioxide, and diluted with water, giving a precipitate of 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-carboxylic acid which formed colourless prismatic needles, m. p. and mixed m. p. 204° (decomp.), from acetic acid.

On treatment with phosphorus pentachloride (2·6 g.) in chloroform (130 ml.) for ½ hour at room temperature and then at 50° for 10 minutes, this acid (4 g.) was converted into the acid chloride which was left as a light-green solid after the evaporation of the solvent and phosphoryl chloride in a vacuum. A suspension of this product in ether (100 ml.) was slowly added to ethereal diazomethane (from 20·6 g. of nitrosomethylurea and 250 ml. of ether) at 0°, the mixture was kept at room temperature for 48 hours, and the resulting crystalline *diazo-ketone* was isolated and recrystallised from benzene–light petroleum (b. p. 40—60°), forming yellow prisms (2·4 g.), m. p. 159° (decomp.) (Found: N, 7·5. $C_{13}H_{12}O_5N_2$ requires N, 8·0%). A further 0·4 g. of less pure product was obtained by evaporation of the ethereal liquor in a vacuum.

3-(3 : 4-*Dimethoxyphenyl*)-6-*methoxycoumarone*-2-*acetic Acid* (VIII).—An intimate mixture of 3-(3 : 4-dimethoxyphenyl)-2-formyl-6-methoxycoumarone (10 g.), hippuric acid (6 g.), sodium acetate (5 g.), and acetic anhydride (50 ml.) was heated on the steam-bath for 15 minutes, cooled, and treated with 50% alcohol (200 ml.). ½ Hour later the resulting *azlactone* was collected, well washed with cold 95% alcohol, and crystallised from benzene, forming small brilliant red needles (13·9 g.), m. p. 219° (Found: N, 3·4. $C_{21}H_{17}O_6N$ requires N, 3·1%). This compound (10 g.) was hydrolysed with boiling 10% aqueous sodium hydroxide (180 ml.) for 5 hours and the orange-brown hydrolysate cooled, diluted with water (120 ml.), and saturated with sulphur dioxide at room temperature. Next day the precipitate of benzoic acid was removed and the aqueous liquor mixed with concentrated hydrochloric acid (50 ml.) and heated on the steam-bath for 2 hours. On cooling, the reaction mixture deposited 3-(3 : 4-*dimethoxyphenyl*)-6-*methoxycoumarone*-2-*pyruvic acid* (VII) which separated from dilute methanol as a *hydrate* in tiny yellow needles (5 g.), m. p. 195—196° (decomp.), having a violet ferric reaction in alcohol (Found: C, 62·3; H, 5·1. $C_{20}H_{18}O_7.H_2O$ requires C, 61·9; H, 5·2. Found, in a specimen dried in a high vacuum at 100°: C, 64·8; H, 4·9. $C_{20}H_{18}O_7$ requires C, 64·9; H, 4·9%). The *oxime* of this pyruvic acid formed clusters of colourless needles, m. p. 146°, from dilute methanol (Found: N, 3·8. $C_{20}H_{19}O_7N$ requires N, 3·6%).

10% Hydrogen peroxide (15 ml.) was added dropwise to a stirred solution of 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-pyruvic acid (5 g.) in 5% aqueous sodium hydroxide (100 ml.) maintained at 0° and the mixture then kept at room temperature for 20 minutes, cooled to 0°, and acidified with dilute hydrochloric acid, giving a precipitate of 3-(3 : 4-*dimethoxyphenyl*)-6-*methoxycoumarone*-2-*acetic acid* (VIII) which crystallised from dilute alcohol (charcoal) in almost colourless needles (3·5 g.), m. p. 178°, and had a deep-red sulphuric acid reaction. Sublimation of this material at 170°/0·2 mm. gave the colourless acid, m. p. 178° (Found: C, 66·3; H, 5·3. $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%). It is readily soluble in alcohol, acetone, ethyl acetate, benzene, or chloroform and insoluble in light petroleum. Treatment of the compound (3·3 g.) with phosphorus pentachloride (2·1 g.) in chloroform (150 ml.) at room temperature with subsequent removal of the solvent and phosphoryl chloride in a vacuum gave the acid chloride which reacted with ammonia to give the *amide*, forming colourless prismatic needles, m. p. 190°, from dilute alcohol (Found: N, 4·2. $C_{19}H_{19}O_5N$ requires N, 4·1%).

4′-*Hydroxy*-6 : 6′ : 7′-*trimethoxynaphtho*(2′ : 1′-2 : 3)*coumarone* (IX).—Phosphoric oxide (5 g.) was added portion-wise to a solution of 3-(3 : 4-dimethoxyphenyl)-6-methoxycoumarone-2-acetic acid (1 g.) in hot benzene (30 ml.) during 3 minutes and the mixture then heated under reflux for 3 hours, cooled, treated with ice (150 g.), and extracted with ether (150 ml. × 3). After having been washed with aqueous sodium hydrogen carbonate and then water, the combined extracts were dried and evaporated, leaving 4′-*hydroxy*-6 : 6′ : 7′-*trimethoxynaphtho*(2′ : 1′-2 : 3)*coumarone* as a pale brown crystalline solid. Recrystallised from ethyl acetate, this compound was obtained in almost colourless prisms (0·25 g.), m. p. 195—196°, soluble in warm benzene or ethyl acetate, sparingly soluble in hot alcohol, and giving a deep-red and a green colour respectively with cold and warm concentrated sulphuric acid (Found: C, 70·2; H, 5·1. $C_{21}H_{18}O_6$ requires C, 70·4; H, 4·9%). In alkaline solution the naphthol readily reacted with benzene- and with α-naphthalene-diazonium chloride to give red azo-dyes. The *p-nitrobenzoate* crystallised from acetic acid in clusters of yellow, elongated rectangular plates, m. p. 193° (Found: N, 3·1. $C_{28}H_{21}O_8N$ requires N, 3·0%).

2-*Hydroxy*-4 : 4′-*dimethoxybenzophenone*.—2 : 4-Dihydroxy-4′-methoxybenzophenone was prepared by the condensation of resorcinol (16 g.) and anisoyl chloride (25 g.) with aluminium chloride (27 g.) in

nitrobenzene (250 ml.) during 48 hours and, on isolation in the usual manner, crystallised from dilute alcohol in pale yellow needles (26 g.), m. p. 160°, identical with a specimen, m. p. 160°, obtained in poor yield by the method of Komarowsky and Kostanecki (*Ber.*, 1894, **27**, 2009) who, however, give m. p. 165°. The ketone had an intense red-brown ferric reaction in alcohol. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate–light petroleum in small orange-red prisms, m. p. 264—265° (Found : N, 13·6. $C_{26}H_{14}O_7N_4$ requires N, 13·2%).

Methyl iodide (5·5 ml.) was added portion-wise to a solution of 2 : 4-dihydroxy-4'-methoxybenzophenone (20 g.) and potassium carbonate (30 g.) in boiling acetone (120 ml.) during 1 hour and the mixture then heated under reflux for 45 minutes. On isolation, the resulting 2-*hydroxy*-4 : 4'-*dimethoxybenzophenone* formed very pale yellow needles (18·7 g.), m. p. 116°, from light petroleum (b. p. 80—100°) or dilute acetone, having an intense red-brown ferric reaction in alcohol (Found : C, 69·4; H, 5·4. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in deep-red prisms, m. p. 238° (Found : N, 13·2. $C_{21}H_{18}O_7N_4$ requires N, 12·8%).

2-*Anisoyl*-5-*methoxyphenoxyacetic Acid*.—The interaction of 2-hydroxy-4 : 4'-dimethoxybenzophenone (10 g.) and ethyl bromoacetate (8 ml.) in boiling acetone containing potassium carbonate (25 g.) in the course of 6 hours gave rise to *ethyl* 2-*anisoyl*-5-*methoxyphenoxyacetate* which crystallised from light petroleum (b. p. 60—80°) or dilute alcohol in long colourless needles (12·2 g.), m. p. 80°, having a negative ferric reaction in alcohol (Found : C, 66·5; H, 5·9. $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·8%). On hydrolysis with a boiling solution of potassium hydroxide (20 g.) in methanol (100 ml.) and water (60 ml.) during 30 minutes, followed by removal of the greater part of the methanol in a vacuum and acidification of the cooled residue with dilute hydrochloric acid, this ester (33 g.) gave rise to 2-*anisoyl*-5-*methoxyphenoxyacetic acid* which formed colourless needles (27 g.), m. p. 139°, from dilute alcohol or benzene–light petroleum (b. p. 60—80°) (Found : C, 64·4; H, 4·8. $C_{17}H_{16}O_6$ requires C, 64·6; H, 5·1%).

6-*Methoxy*-3-*p*-*methoxyphenylcoumarone*.—A mixture of 2-anisoyl-5-methoxyphenoxyacetic acid (10 g.), sodium acetate (20 g.), and acetic anhydride (100 ml.) was heated at 160° for ½ hour and poured into water (500 ml.). Next day the solid was collected, thoroughly triturated with aqueous sodium hydrogen carbonate, and crystallised from dilute acetic acid (charcoal), giving 6-*methoxy*-3-*p*-*methoxyphenylcoumarone* in long colourless needles (6·3 g.), m. p. 60°, having a red-brown sulphuric acid reaction (Found : C, 75·4; H, 5·7. $C_{18}H_{16}O_3$ requires C, 75·6; H, 5·5%).

2-*Formyl*-6-*methoxy*-3-*p*-*methoxyphenylcoumarone*.—Prepared by the interaction of 6-methoxy-3-*p*-methoxyphenylcoumarone (5 g.), hydrogen cyanide (7·5 ml.), and zinc chloride (2 g.) in ether (100 ml.), saturated at 0° with hydrogen chloride, the crystalline aldimine derivative was hydrolysed with water (200 ml.) on the steam-bath for ½ hour, giving 2-*formyl*-6-*methoxy*-3-*p*-*methoxyphenylcoumarone* which separated from alcohol in colourless needles (5 g.), m. p. 167° (Found : C, 72·5; H, 5·0. $C_{19}H_{14}O_4$ requires C, 72·3; H, 5·0%). The brown-red solution of this aldehyde in concentrated sulphuric acid rapidly changed to yellow-green and on being warmed and diluted with water it then became green and then deep blue. The 2 : 4-*dinitrophenylhydrazone* formed dull red needles, m. p. 255° after sintering at 230°, from nitrobenzene–alcohol (Found : N, 12·0. $C_{25}H_{18}O_7N_4$ requires N, 12·1%).

6-*Methoxy*-3-*p*-*methoxyphenylcoumarone*-2-*carboxylic Acid*.—(*a*) Cyclisation of ethyl 2-anisoyl-5-methoxyphenoxyacetate (5 g.) with sodium ethoxide (from 0·4 g. of sodium) in boiling alcohol (50 ml.) during 1 hour followed by dilution of the reaction mixture with water (200 ml.) gave *ethyl* 6-*methoxy*-3-*p*-*methoxyphenylcoumarone*-2-*carboxylate* which separated from alcohol in long colourless needles (1·4 g.), m. p. 98°, having a reddish-orange sulphuric acid reaction (Found : C, 69·7; H, 5·8. $C_{21}H_{20}O_5$ requires C, 70·0; H, 5·5%). On hydrolysis with boiling 5% aqueous-methanolic potassium hydroxide (10 ml.) for ½ hour this ester (0·3 g.) gave rise to 6-*methoxy*-3-*p*-*methoxyphenylcoumarone*-2-*carboxylic acid*, forming colourless needles (0·2 g.), m. p. 223° (decomp.), from ethyl acetate (Found : C, 68·6; H, 4·8. $C_{19}H_{16}O_5$ requires C, 68·5; H, 4·7%). A mixture of this acid (0·5 g.), m. p. and mixed m. p. 223° (decomp.), and 6-methoxy-3-*p*-methoxyphenylcoumarone (1·1 g.) was obtained by the addition of an excess of dilute hydrochloric acid to the alkaline filtrate from the crude ester. The compounds were separated by fractional crystallisation from alcohol and ethyl acetate.

(*b*) A mixture of 2-formyl-6-methoxy-3-*p*-methoxyphenylcoumarone (0·5 g.), 30% hydrogen peroxide (5 ml.), 5% aqueous sodium hydroxide (10 ml.), and acetone (50 ml.) was kept at 40° for 75 minutes with the addition of more 30% hydrogen peroxide (5 ml.) after 1 hour. After the removal of the acetone, the cooled reaction mixture was diluted with water (50 ml.), filtered to remove a little tarry material, and acidified with dilute hydrochloric acid, giving a precipitate of 6-methoxy-3-*p*-methoxyphenylcoumarone-2-carboxylic acid, m. p. and mixed m. p. 223° (decomp.) after purification.

6-*Methoxy*-3-*p*-*methoxyphenylcoumarone*-2-*acetic Acid*.—An intimate mixture of 2-formyl-6-methoxy-3-*p*-methoxyphenylcoumarone (10 g.), hippuric acid (6·5 g.), sodium acetate (3 g.), and acetic anhydride (50 ml.) was heated on the steam-bath for 30 minutes, cooled, and treated with 50% alcohol (100 ml.). ½ Hour later the *azlactone* was collected and crystallised from benzene, forming bright orange needles (12·4 g.), m. p. 226° (Found : N, 3·4. $C_{26}H_{19}O_5N$ requires N, 3·3%). This compound (10 g.) was hydrolysed with boiling 10% aqueous potassium hydroxide (150 ml.) for 5½ hours and the resulting 6-*methoxy*-3-*p*-*methoxyphenylcoumarone*-2-*pyruvic acid* isolated by the sulphur dioxide method and crystallised from dilute acetic acid, forming pale yellow, elongated rectangular prisms (7 g.), m. p. 225—226° (decomp.), which gave a violet ferric reaction in alcohol (Found : C, 66·7; H, 4·8. $C_{19}H_{16}O_6$ requires C, 67·1; H, 4·7%). The *oxime* separated from ethyl acetate–light petroleum (b. p. 60—80°) in small colourless rods, m. p. 164° (decomp.) (Found : N, 4·0. $C_{19}H_{17}O_6N$ requires N, 3·9%).

Oxidation of this pyruvic acid (5 g.), dissolved in 5% aqueous sodium hydroxide (100 ml.), with 30% hydrogen peroxide (10 ml., added during 15 minutes) at room temperature, followed by acidification of the solution with dilute hydrochloric acid gave 6-*methoxy*-3-*p*-*methoxyphenylcoumarone*-2-*acetic acid* which separated from dilute alcohol and then benzene–light petroleum (b. p. 60—80°) in almost colourless

needles (3·7 g.), m. p. 169—170°, having a deep orange-brown sulphuric acid reaction (Found: C, 69·2; H, 5·1. $C_{14}H_{12}O_3$ requires C, 69·2; H, 5·1%). It is readily soluble in ethyl acetate or acetone and moderately soluble in methanol, acetic acid, or benzene. Interaction of the acid with a molecular proportion of phosphorus pentachloride in chloroform furnished the acid chloride as a solid which on treatment with ammonia yielded the *amide*, forming tiny colourless prisms, m. p. 210°, from benzene–light petroleum (b. p. 60—80°) (Found: N, 4·8. $C_{14}H_{11}O_4N$ requires N, 4·5%).

4'-Hydroxy-6:6'-dimethoxynaphtho(2':1'-2:3)coumarone.—Cyclisation of 6-methoxy-3-*p*-methoxyphenylcoumarone-2-acetic acid (0·6 g.) with phosphoric oxide (4 g.) in boiling benzene (20 ml.) during 5 hours and subsequent treatment of the reaction mixture with ice (200 g.), gave the desired *naphthol* which was isolated with chloroform and crystallised from acetic acid, forming colourless tiny needles (0·2 g.), m. p. 179—180° and giving a deep-red and a green colour with cold and warm concentrated sulphuric acid respectively (Found: C, 73·4; H, 4·9. $C_{19}H_{14}O_4$ requires C, 73·5; H, 4·8%). In alkaline solution this naphthol gave red azo-dyes with benzene- and α-naphthalene-diazonium chloride.

2-Hydroxy-4:3'-dimethoxybenzophenone.—A mixture of resorcinol (9 g.), *m*-anisoyl chloride (13 g.), aluminium chloride (15 g.), and nitrobenzene (120 ml.) was kept at room temperature for 48 hours, and then treated with ice (100 g.) and concentrated hydrochloric acid (200 ml.). After the removal of the nitrobenzene with steam 2:4-*dihydroxy*-3'-*methoxybenzophenone* remained in the acidic liquor as a solid and, on crystallisation from dilute alcohol, formed pale yellow, elongated rectangular prisms (16 g.), m. p. 176°, having a red-brown ferric reaction (Found: C, 69·2; H, 5·0. $C_{14}H_{12}O_4$ requires C, 68·9; H, 4·9%). The condensation of *m*-anisic acid (5 g.) and resorcinol (4 g.) with zinc chloride (5 g.) at 160° for 10 minutes, according to the method of Nencki, gave a poor yield of the same benzophenone (0·3 g.), m. p. and mixed m. p. 176°, after purification. The 2:4-*dinitrophenylhydrazone* separated from ethyl acetate in masses of orange prisms, m. p. 285—287° (Found: N, 13·1. $C_{20}H_{14}O_7N_4$ requires N, 13·2%).

A solution of methyl iodide (9 ml.) was added dropwise in the course of 1 hour to a boiling solution of the ketone (30 g.) in acetone (200 ml.) containing potassium carbonate (45 g.), and the mixture then heated under reflux for 1 hour. On isolation the resulting 2-*hydroxy*-4:3'-*dimethoxybenzophenone* crystallised from methanol in cream needles (22 g.), m. p. 66°, having a red-brown ferric reaction (Found: C, 69·8; H, 5·7. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%). This compound is readily soluble in acetone, ethyl acetate, benzene, or carbon tetrachloride and sparingly soluble in boiling light petroleum. The 2:4-*dinitrophenylhydrazone* formed clusters of brilliant red, tiny, elongated prisms, m. p. 204°, from ethyl acetate (Found: N, 12·6. $C_{21}H_{16}O_7N_4$ requires N, 12·8%).

2-m-Anisoyl-5-methoxyphenoxyacetic Acid.—The interaction of 2-hydroxy-4:3'-dimethoxybenzophenone (20 g.) and ethyl bromoacetate (16 ml.) in boiling acetone (200 ml.) containing potassium carbonate (50 g.) during 5 hours gave rise to *ethyl* 2-m-*anisoyl*-5-*methoxyphenoxyacetate*, forming colourless irregular prisms (24 g.), m. p. 76°, from dilute methanol, soluble in the usual organic solvents except light petroleum (Found: C, 66·6; H, 6·0. $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·8%). On hydrolysis with 10% aqueous-methanolic potassium hydroxide (20 ml.) during ½ hour this ester (4·5 g.) yielded the corresponding *acid* which separated from ethyl acetate–light petroleum (b. p. 60—80°) in long needles (4 g.), m. p. 80—81°, easily soluble in alcohol, acetone, or ethyl acetate and sparingly soluble in warm water (Found: C, 64·5; H, 5·2. $C_{17}H_{16}O_6$ requires C, 64·6; H, 5·1%).

6-Methoxy-3-m-methoxyphenylcoumarone.—Cyclisation of the foregoing phenoxyacetic acid (6 g.) with acetic anhydride (60 ml.) and sodium acetate (12 g.) at 150° for ½ hour gave rise to 6-*methoxy*-3-m-*methoxyphenylcoumarone* which crystallised from methanol in long, colourless needles (4 g.), m. p. 55°, having a yellow orange sulphuric acid reaction (Found: C, 75·8; H, 5·7. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

Prepared from this coumarone (5 g.), hydrogen cyanide (7 ml.) and zinc chloride (2 g.) in ether (70 ml.) saturated with hydrogen chloride during 24 hours, the crystalline aldimine complex was hydrolysed with water (250 ml.) on the steam-bath for ½ hour, giving 2-*formyl*-6-*methoxy*-3-m-*methoxyphenylcoumarone* which formed yellow irregular prisms (4·1 g.), m. p. 92°, from alcohol (Found: C, 72·0; H, 4·8. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%). The yellow solution of this compound in concentrated sulphuric acid became darker on warming and then on dilution with water changed to blue-green. The 2:4-*dinitrophenylhydrazone* separated from acetic acid in dull red needles, m. p. 226—227° after sintering at 220° (Found: N, 12·0. $C_{23}H_{18}O_7N_4$ requires N, 12·1%).

6-Methoxy-3-m-methoxyphenylcoumarone-2-acetic Acid.—(*a*) A mixture of the aforementioned aldehyde (3 g.), hippuric acid (2 g.), sodium acetate (1 g.), and acetic anhydride (20 ml.) was heated on the steam-bath for ½ hour, cooled, and diluted with 50% alcohol (80 ml.). Crystallised from benzene, the resulting *azlactone* formed small, bright orange, rectangular prisms (3·3 g.), m. p. 226° (Found: N, 3·6. $C_{26}H_{19}O_5N$ requires N, 3·3%). On hydrolysis with boiling 10% aqueous sodium hydroxide (120 ml.) for 5½ hours this compound (9 g.) gave 6-*methoxy*-3-m-*methoxyphenylcoumarone*-2-*pyruvic acid* which was isolated by the sulphur dioxide method and crystallised from ethyl acetate–light petroleum (b. p. 60—80°), forming yellow prisms (1 g.), m. p. 170—172° (decomp.), and giving a violet ferric reaction in alcohol (Found: C, 66·9; H, 4·5. $C_{19}H_{16}O_5$ requires C, 67·1; H, 4·7%). Oxidation of the pyruvic acid (0·1 g.), dissolved in 5% sodium hydroxide (5 ml.), with 10% hydrogen peroxide (5 ml.) at room temperature in the course of 1 hour furnished 6-*methoxy*-3-m-*methoxyphenylcoumarone*-2-*acetic acid* which separated from light petroleum (b. p. 80—100°) in colourless needles, m. p. 141—142° (Found: C, 69·2; H, 5·1. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%). On being warmed the deep-yellow solution of the acid in concentrated sulphuric acid became deep green.

(*b*) A mixture of ethyl 2-*m*-anisoyl-5-methoxyphenoxyacetate (18 g.), alcohol (100 ml.), and sodium ethoxide (from 1·4 g. of sodium) was heated under reflux for 45 minutes and diluted with water (400 ml.). Next day 6-*methoxy*-3-m-*methoxyphenylcoumarone*-2-*carboxylic acid* was precipitated from the solution with dilute hydrochloric acid and crystallised from benzene, forming small, colourless prisms (7·5 g.),

m. p. 192° (decomp.), which with concentrated sulphuric acid gave a deep yellow colour which changed to a deep green on warming (Found: C, 68·2; H, 4·6. $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%). This acid (5 g.) was converted into the acid chloride by means of phosphorus pentachloride (3·7 g.) in chloroform (100 ml.) and, after the removal of the solvent and phosphoryl chloride, the product was obtained as a solid which was immediately dissolved in benzene (50 ml.) and treated with an excess of ethereal diazomethane (from 20·6 g. of nitrosomethylurea) at 0°. Next day the solution was filtered to remove traces of solid, the solvents were removed in a vacuum, and the residual *diazo-ketone* recrystallised from benzene–light petroleum (b. p. 40—60°), forming yellow elongated prisms, m. p. 124—126° (decomp.) (Found: N, 8·4. $C_{18}H_{14}O_4N_2$ requires N, 8·7%). A solution of the diazo-ketone in dioxan (100 ml.) was added drop-wise to a well-stirred mixture of 10% aqueous silver nitrate (40 ml.) and concentrated aqueous ammonia (25 ml.) kept at 70°. After having been kept at this temperature for 1 hour the reaction mixture was allowed to cool and next day *6-methoxy-3-m-methoxyphenylcoumarone-2-acetamide* was isolated from the reaction mixture with ether and crystallised from ethyl acetate–light petroleum (b. p. 60—80°) and then benzene, forming colourless needles (1·8 g.), m. p. 153°, readily soluble in alcohol, ethyl acetate, or chloroform (Found: N, 4·2. $C_{18}H_{17}O_4N$ requires N, 4·3%). This amide (1·5 g.) was hydrolysed with boiling 10% aqueous-alcoholic potassium hydroxide (15 ml.) during 9 hours and the cooled solution was diluted with water (100 ml.), extracted with ether to remove traces of non-acidic impurities, and acidified with hydrochloric acid, giving 6-methoxy-3-*m*-methoxyphenylcoumarone-2-acetic acid (1·3 g.), m. p. and mixed m. p. 141—142° after recrystallisation.

4′-Hydroxy-6′-dimethoxynaphtho(2′ : 1′-2 : 3)*coumarone*.—On being heated with phosphoric oxide (4 g.) in boiling benzene (30 ml.) during 3 hours 6-methoxy-3-*m*-methoxyphenylcoumarone-2-acetic acid (0·8 g.) gave rise to *4′-hydroxy-6′-dimethoxynaphtho*(2′ : 1′-2 : 3)*coumarone* which was isolated with ether and freed from traces of acidic material by means of aqueous sodium hydrogen carbonate. Recrystallised from benzene–light petroleum (b. p. 60—80°), this compound formed pale yellow, elongated prisms (0·3 g.), m. p. 158—159°, easily soluble in chloroform and moderately soluble in benzene, acetic acid, or warm alcohol (Found: C, 73·4; H, 4·8. $C_{19}H_{16}O_4$ requires C, 73·5; H, 4·8%). In alkaline solution the naphthol reacted with benzene- and α-naphthalene-diazonium chloride, forming red azo-dyes. With sulphuric acid it gave a deep-red and then a green colour.

2′-Carboxy-2-hydroxy-5-methoxybenzophenone.—Methyl iodide (7·5 ml.) was added during 1 hour to a boiling solution of 2′-carbethoxy-2 : 4-dihydroxybenzophenone (Desai and Figueredo, *Proc. Indian Acad. Sci.*, 1941, **14**, *A*, 605; Tambor, *Ber.*, 1910, **43**, 1882) (25 g.) in acetone (200 ml.) containing potassium carbonate (40 g.), and the mixture then heated under reflux for 1 hour. On isolation, *2′-carbethoxy-2-hydroxy-4-methoxybenzophenone* (X; R = H) crystallised from light petroleum (b. p. 80—100°) in yellow irregular prisms (23·8 g.), m. p. 100°, having a red-brown ferric reaction in alcohol (Found: C, 67·8; H, 5·2. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). Hydrolysis of this compound with 10% aqueous methanolic potassium hydroxide for ½ hour gave rise to 2′-carboxy-2-hydroxy-4-methoxybenzophenone, m. p. 165°, identical with a specimen prepared by the method of Desai and Figueredo (*loc. cit.*).

2-o-Carboxybenzoyl-5-methoxyphenoxyacetic Acid (XI; R = R′ = H).—A mixture of 2′-carbethoxy-2-hydroxy-4-methoxybenzophenone (22 g.), ethyl bromoacetate (16 ml.), potassium carbonate (70 g.), and acetone (200 ml.) was heated under reflux for 5 hours. On isolation the resulting product was obtained as a yellow syrup which was hydrolysed with boiling 10% aqueous-methanolic potassium hydroxide (200 ml.) for ½ hour. After the removal of the greater part of the methanol and the dilution of the residual hydrolysate with water, *2-o-carboxybenzoyl-5-methoxyphenoxyacetic acid* was precipitated with hydrochloric acid and crystallised from alcohol–light petroleum (b. p. 60—80°), forming colourless flat prisms (23 g.), m. p. 177—178° (Found: C, 62·0; H, 4·4. $C_{17}H_{14}O_7$ requires C, 61·8; H, 4·2%), soluble in the usual organic solvents except light petroleum.

3-o-Carboxyphenyl-6-methoxycoumarone (XII; R = OH, R′ = H).—On being heated with sodium acetate (30 g.) and acetic anhydride (100 ml.) at 160° for ½ hour 2-*o*-carboxybenzoyl-5-methoxyphenoxyacetic acid (10 g.) gave rise to *3-o-carboxyphenyl-6-methoxycoumarone* which was extracted from the crude reaction product with hot light petroleum (b. p. 80—100°) and then crystallised from the same solvent, forming colourless rectangular prisms (3·8 g.), m. p. 135°, having a deep blue-green sulphuric acid reaction (Found: C, 71·6; H, 4·5. $C_{16}H_{12}O_4$ requires C, 71·7; H, 4·5%).

3-o-Carboxymethylphenyl-6-methoxycoumarone (XIII; R = H).—The foregoing acid (5 g.) was added in portions to a mixture of benzene (50 ml.), thionyl chloride (2·6 ml.), and pyridine (3 drops) at room temperature during 15 minutes. ½ Hour later the reaction mixture was warmed to 40—45° for 15 minutes and then evaporated in a vacuum with the addition of more benzene (20 ml.) to remove traces of residual thionyl chloride. A solution of the residual acid chloride in benzene (50 ml.) was added drop-wise during 30 minutes to well-stirred ethereal diazomethane (from 20·6 g. of nitrosomethylurea and 200 ml. of ether) kept at 0° and, after having been kept at room temperature for 24 hours, the reaction mixture was evaporated in a vacuum, leaving the *diazo-ketone* (XII; R = CHN_2, R′ = H) as a yellow crystalline mass. Recrystallised from benzene–light petroleum (b. p. 60—80°), this compound formed pale yellow needles, m. p. 85—87° (Found: N, 9·8. $C_{19}H_{14}O_3N_2$ requires N, 9·6%).

A solution of this diazo-ketone in dioxan (50 ml.) was added drop-wise during 35 minutes to a well-stirred mixture of 10% silver nitrate (40 ml.) and concentrated aqueous ammonia (25 ml.) at 60—70° and, after having been kept at this temperature for 1½ hours, the reaction mixture was filtered and allowed to cool, depositing *3-o-carbamylmethylphenyl-6-methoxycoumarone* which formed colourless needles (3 g.), m. p. 148°, from benzene–light petroleum (b. p. 60—80°) (Found: N, 4·9. $C_{18}H_{15}O_3N$ requires N, 5·0%). Hydrolysis of this amide (2 g.) with boiling 10% alcoholic potassium hydroxide (20 ml.) for 16 hours, followed by dilution of the hydrolysate with water (100 ml.) and acidification with dilute hydrochloric acid, gave *3-o-carboxymethylphenyl-6-methoxycoumarone* which separated from dilute methanol in colourless needles (2 g.), m. p. 125°, having a deep red sulphuric acid reaction (Found: C, 72·3; H, 5·1. $C_{18}H_{14}O_4$ requires C, 72·4; H, 5·0%). This acid was soluble in alcohol, ethyl acetate, or benzene and sparingly soluble in light petroleum.

3′-*Hydroxy*-6-*methoxynaphtho*(2′ : 1′-2 : 3)*coumarone* (XIV).—A solution of the foregoing acetic acid (1 g.) in concentrated sulphuric acid (20 ml.) was kept at room temperature for ½ hour and poured on ice (100 g.). Crystallised from benzene or dilute alcohol, the resulting precipitate gave the *naphthocoumarone* in colourless prismatic needles (0·5 g.), m. p. 163°, readily soluble in alcohol or acetic acid and moderately soluble in ethyl acetate or benzene (Found: C, 77·2; H, 4·7. $C_{17}H_{12}O_3$ requires C, 77·3; H, 4·5%). On being warmed with alcoholic potassium hydroxide and a drop of chloroform this phenol gave a deep-blue colour which slowly became green and then yellow. With benzene- and α-naphthalene-diazonium chloride it gave red azo-dyes. The *p-nitrobenzoate* crystallised from ethyl acetate in yellow plates, m. p. 191° (Found: N, 3·4. $C_{24}H_{15}O_5N$ requires N, 3·4%).

2′-*Carbethoxy*-2-*hydroxy*-4 : 4′ : 5′-*trimethoxybenzophenone* (X; R = OMe).—Prepared by the interaction of resorcinol (5 g.), *m*-hemipinic anhydride (Perkin *et al.*, *J.*, 1925, **127**, 195; Perkin, *J.*, 1916, **109**, 889) (8 g.), and aluminium chloride (10 g.) in nitrobenzene (100 ml.) at room temperature for 48 hours, then at 60° for 1½ hours, and finally at 100° for 10 minutes. **2′-*carboxy*-2 : 4-*dihydroxy*-4′ : 5′-*dimethoxybenzophenone*** separated from ethyl acetate–light petroleum (b. p. 60—80°) in pale yellow prisms (10 g.), m. p. 255° (decomp.), having a red-brown ferric reaction in alcohol (Found: C, 60·4; H, 4·5. $C_{18}H_{18}O_7$ requires C, 60·4; H, 4·4%). Esterification of this acid (9·5 g.) with boiling alcohol (50 ml.) containing concentrated sulphuric acid during 4 hours yielded the *ethyl* ester which formed yellow needles (7·5 g.), m. p. 171°, from dilute alcohol, having a red-brown ferric reaction (Found: C, 62·5; H, 5·3. $C_{19}H_{20}O_7$ requires C, 62·4; H, 5·2%). The ester is readily soluble in the usual organic solvents except light petroleum.

Methyl iodide (3 ml. in 20 ml. of acetone) was added gradually during 45 minutes to a solution of this ester (8·5 g.) in boiling acetone (100 ml.), containing potassium carbonate (15 g.), and the mixture then heated for 1 hour. On isolation the resulting **2′-*carbethoxy*-2-*hydroxy*-4 : 4′ : 5′-*trimethoxybenzophenone*** (X; R = OMe) crystallised from dilute alcohol in yellow irregular prisms (8 g.), m. p. 110°, having a red-brown ferric reaction (Found: C, 63·6; H, 5·8. $C_{19}H_{20}O_7$ requires C, 63·4; H, 5·6%). Hydrolysis of this ester (0·3 g.) with boiling 5% aqueous-methanolic potassium hydroxide (10 ml.) for 15 minutes gave rise to 2′-carboxy-2-hydroxy-4 : 4′ : 5′-trimethoxybenzophenone which separated from ethyl acetate–light petroleum (b. p. 60—80°) in masses of pale yellow prisms (0·2 g.), m. p. 212° (Found: C, 61·4; H, 4·7. Calc. for $C_{17}H_{16}O_7$: C, 61·5; H, 4·8%) (compare Ray *et al.*, *loc. cit.*, who give m. p. 203°).

Brazilinic Acid (XI; R = H, R′ = OMe).—A mixture of 2′-carbethoxy-2-hydroxy-4 : 4′ : 5′-trimethoxybenzophenone (8 g.), ethyl bromoacetate (5 ml.), potassium carbonate (24 g.), and acetone (100 ml.) was heated under reflux for 5 hours. On isolation the resulting ethyl brazilinate was obtained as a yellow syrup which was hydrolysed with boiling 10% aqueous-methanolic potassium hydroxide (100 ml.) during ½ hour. After the removal of the methanol in a vacuum the residue was mixed with ice-water (200 ml.) and acidified with dilute hydrochloric acid, giving a precipitate of brazilinic acid (8·2 g.) which was collected 48 hours later. Crystallised from dilute acetic acid, the compound formed colourless prisms, m. p. 208—209° (Found: C, 58·3; H, 4·6. Calc. for $C_{19}H_{18}O_8$: C, 58·5; H, 4·6%) (cf. Perkin and Robinson, *J.*, 1908, **93**, 515; Ray *et al.*, *loc. cit.*).

3-(2-*Carboxymethyl*-4 : 5-*dimethoxyphenyl*)-6-*methoxycoumarone* (XIII; R = OMe).—A mixture of brazilinic acid (9 g.), potassium acetate (27 g.), and acetic anhydride (90 ml.) was kept at 150° for 45 minutes, cooled, and treated with water (500 ml.). Next day the precipitated **3-(2-*carboxy*-4 : 5-*dimethoxyphenyl*)-6-*methoxycoumarone*** (XII; R = OH, R′ = OMe) was collected and crystallised from acetic acid, forming pale yellow prismatic needles (4·9 g.), m. p. 210°, easily soluble in chloroform, warm alcohol, or ethyl acetate (Found: C, 65·7; H, 4·9. $C_{19}H_{16}O_6$ requires C, 65·9; H, 4·9%). This acid (5 g.) was converted into the acid chloride by treatment with thionyl chloride (2·5 ml.) and pyridine (3 drops) in benzene (150 ml.) at room temperature for 35 minutes and then on the steam-bath for 15 minutes. After the evaporation of the reaction mixture in a vacuum the residue was dissolved in benzene (30 ml.) and the solution evaporated. Repetition of this process finally gave the acid chloride as a red viscous liquid. A solution of this compound in benzene (50 ml.) was added drop-wise to ethereal diazomethane (from 20 g. of nitrosomethylurea and 200 ml. of ether) at 0° and, after having been kept at room temperature for 24 hours, the reaction mixture was evaporated, leaving the ***diazo-ketone*** (XII; R = CHN_2, R′ = OMe) as an orange-yellow crystalline solid which formed large orange-yellow prisms, m. p. 86—88°, from benzene–light petroleum (b. p. 40—60°) (Found: N, 7·9. $C_{19}H_{16}O_5N_2$ requires N, 8·0%). A solution of this compound in dioxan (50 ml.) was added drop-wise to a well-stirred mixture of 10% silver nitrate (50 ml.) and concentrated aqueous ammonia (25 ml.) kept at 65—70° during 15 minutes and the mixture then kept at this temperature for 2½ hours. From the cooled, filtered reaction mixture **3-(2-*carbamylmethyl*-4 : 5-*dimethoxyphenyl*)-6-*methoxycoumarone*** was isolated with chloroform (100 ml. × 3) and crystallised from dilute methanol, forming colourless prisms (2·2 g.), m. p. 143° (Found: N, 4·4. $C_{19}H_{19}O_5N$ requires N, 4·1%). On hydrolysis with boiling 15% alcoholic potassium hydroxide (50 ml.) for 14 hours, this amide gave rise to **3-(2-*carboxymethyl*-4 : 5-*dimethoxyphenyl*)-6-*methoxycoumarone*** which separated from benzene–light petroleum (b. p. 60—80°) and then dilute methanol in colourless needles (1·7 g.), m. p. 148·5—149·5°, having a deep red sulphuric acid reaction (Found: C, 66·6; H, 5·0. $C_{19}H_{18}O_6$ requires C, 66·9; H, 5·3%).

3′-*Hydroxy*-6 : 6′ : 7′-*trimethoxynaphtho*(2′ : 1′-2 : 3)*coumarone* (**α-*Anhydro*-*O*-*trimethylbrazilone*s**) (IV).—Cyclised by means of concentrated sulphuric acid (25 ml.) at room temperature during ½ hour, the foregoing acetic acid (1·2 g.) furnished α-anhydro-*O*-trimethylbrazilone which was precipitated from the reaction mixture with ice (75 g.) and crystallised from acetic acid, forming large pale brown prisms. Recrystallised from alcohol, this specimen then formed yellow plates (0·8 g.), m. p. 198°, identical with the compound from natural sources (Found: C, 70·2; H, 5·0. Calc. for $C_{19}H_{16}O_5$: C, 70·4; H, 4·9%). On being warmed with a little alcoholic potassium hydroxide containing a drop of chloroform, the synthetic naphthol gave an intense blue colour which slowly changed to green and then yellow-brown. On being warmed the orange-red solution of the naphthol in concentrated sulphuric acid became deep

red. With benzene- and α-naphthalene-diazonium chloride an alkaline solution of the compound gave red azo-dyes. The acetate crystallised from benzene in clusters of colourless elongated plates, m. p. 174—175° (Found: C, 69·0; H, 5·0. Calc. for $C_{21}H_{18}O_4$: C, 68·9; H, 4·9%) (Perkin and Robinson, *J.*, 1909, **95**, 393). Prepared by the method employed by Perkin and Robinson (*loc. cit.*) for the natural derivative, synthetical acetyl-nitro-α-anhydro-*O*-trimethylbrazilone separated from acetic acid in bright yellow needles, m. p. 235° (decomp.) after sintering at 222°, and with concentrated sulphuric acid gave a purple colour which became yellow-brown on the addition of water (Found: N, 3·3. Calc. for $C_{21}H_{17}O_6N$: N, 3·4%).

The p-*nitrobenzoate* of α-anhydro-*O*-trimethylbrazilone formed bright yellow, elongated prisms, m. p. 233—234°, from acetic acid (Found: N, 2·9. $C_{28}H_{19}O_8N$ requires N, 3·0%).

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489. *Acenaphthene Series. Part IV. Two Isomeric Ethylacenaphthenes and their Derivatives.*

By H. E. NÜRSTEN and A. T. PETERS.

The ethylacenaphthene, prepared from acenaphthene by means of ethyl bromide and aluminium chloride, using carbon disulphide as solvent, is shown to be 2-ethylacenaphthene.*

In Part III of this series (*J.*, 1950, 729), it was shown that the butylation of acenaphthene by means of *tert.*-butyl chloride and aluminium chloride in carbon disulphide yielded a mixture of 2-*tert.*-butylacenaphthene* and 2 : 5-di-*tert.*-butylacenaphthene. No such direct substitution in the 2-position of the acenaphthene molecule had been previously observed but it was thought that such *meta*-alkylation would occur also when alkyl halides other than *tert.*-butyl chloride were used.

	Product obtained through 3-acetyl-acenaphthene, m. p.	Product obtained by direct ethylation, m. p.	1-Substituted derivatives. m. p.	Reference.
Ethylacenaphthene	41·5—42·5°	liquid	34·8—35·1° [1]	Fieser and Kilmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1354.
picrate	91—92 [2]	101·5—102·5° [3]	104·7—105·1	" "
quinone	117—119	150—152	128	Buu-Hoï and Cagniant, *Rev. Sci.*, 1943, **81**, 72.
Ethylthionaphthenacenaphthenylindigo	216—217 [3]	204—206 [3]	—	—
Ethylnaphthalic anhydride	164—164·5 [4]	192—193 [4]	—	—
Ethylnaphthalimide	195—196	217—218·5	—	—
Ethylnaphthal-*N*-methylimide	140	113—114	—	—
Carboxynaphthalic anhydride	273—274 [5]	289—290 [5]	297·5—298·5	Fieser and Cason, *J. Amer. Chem. Soc.*, 1939, **61**, 1740.
Carbomethoxynaphthalic anhydride	222 [6]	226—227	191—192	" "

[1] First prepared by Cook, Haslewood, and Robinson, *J.*, 1935, 667. [2] Mixed m. p. below 78°. [3] Mixed m. p. below 180°. [4] Mixed m. p. 141—144°. [5] Mixed m. p. 257—259°. [6] Fieser and Peters, *loc. cit.*

Mayer and Kaufmann (*Ber.*, 1920, **53**, 289) first prepared an ethylacenaphthene, an oil, b. p. 310° (picrate m. p. 95—96°), by treating acenaphthene with ethyl bromide and aluminium chloride in carbon disulphide. They oxidised it to an impure quinone and an ethylnaphthalic

* Richter's numbering of the acenaphthene system is used in this paper as in preceding Parts of the series:

anhydride, m. p. 180°, and thence to a carboxynaphthalic anhydride, m. p. 248°, which they identified with the 4-carboxynaphthalic anhydride, m. p. 243°, obtained by Graebe (*Annalen*, 1903, **327**, 77) by oxidation of 3-acetylacenaphthene. However, Fieser and Peters (*J. Amer. Chem. Soc.*, 1932, **54**, 4347) (*cf.* Dziewoński, Kahl, Koczorowska, and Wulffsohn, *Bull. Acad. Polonaise*, 1933, *A*, 194) showed that pure 4-carboxynaphthalic anhydride melted at 274°, and therefore Mayer and Kaufmann's orientation cannot be accepted as proved.

Fleischer and Wolff (*Ber.*, 1920, **53**, 925) reduced 3-acetylacenaphthene to 3-ethylacenaphthene, m. p. 42·5—43°. This compound they thought to be identical with that prepared by Mayer and Kaufmann. We therefore repeated Mayer and Kaufmann's and Fleischer and Wolff's preparations. The ethylacenaphthenes and numerous new derivatives are compared in the table (p. 2389), which also includes data for 1-ethylacenaphthene and its derivatives taken from the literature. Clearly Mayer and Kaufmann's ethylacenaphthene cannot be the 1- or the 3-isomer. As on oxidation it yielded an ethylnaphthalic anhydride, it was not the 7-isomer. By elimination, therefore, the direct ethylation of acenaphthene had produced mainly 2-ethylacenaphthene.

In preliminary experiments to show the effect of aluminium chloride on 3-ethylacenaphthene, considerable dealkylation to acenaphthene took place and there was some evidence of the formation of 2-ethylacenaphthene.

Research on alkylacenaphthenes is being continued.

Experimental.

(M. p.s are corrected. Microanalyses were carried out by Drs. Weiler and Strauss, Oxford.)

3-Acetylacenaphthene.—This was prepared by Fieser and Hershberg's method (*J. Amer. Chem. Soc.*, 1939, **61**, 1272), which was much more satisfactory than that of Graebe (*loc. cit.*), the yield of crude 3-acetylacenaphthene, m. p. 52—56° (Found: C, 85·7; H, 6·0. Calc. for $C_{14}H_{12}O$: C, 85·7; H, 6·1%), being 58%. The 2:4-*dinitrophenylhydrazone*, m. p. 246°, crystallised from pyridine in red needles and plates with a metallic lustre (Found: N, 14·9. $C_{20}H_{14}O_4N_4$ requires N, 15·4%).

4-Acetylnaphthalic Anhydride.—Crude 3-acetylacenaphthene (10 g.) was dissolved in boiling acetic acid (300 c.c.), sodium dichromate (40 g.) was added gradually, and the solution was refluxed for 5 hours. The anhydride (8·8 g., 72%) recrystallised from acetic acid (charcoal) in colourless needles, m. p. 196—197° (Found: C, 69·8; H, 3·4. Calc. for $C_{14}H_8O_4$: C, 70·0; H, 3·3%). Dziewoński and Piasecki (*Bull. Acad. Polonaise*, 1932, *A*, 287) recorded m. p. 191—192°. The imide separated from absolute alcohol in almost colourless needles, m. p. 273° (Found: N, 6·2. Calc. for $C_{14}H_9O_3N$: N, 5·9%). Dziewoński and Piasecki recorded m. p. 270—272°.

Oxidation of 4-Acetylnaphthalic Anhydride.—(a) *With potassium permanganate.* 4-Acetylnaphthalic anhydride (0·5 g.), dissolved in hot 1% aqueous sodium hydroxide (50 c.c.), was oxidised by the addition of a boiling solution of potassium permanganate (1 g.) in water (25 c.c.). The mixture was boiled for a short time and any excess of permanganate was destroyed by the addition of a little alcohol. After filtration and acidification, the filtrate was evaporated to small bulk and extracted with ether. On concentration of the extract and cooling, pale yellow needles (0·15 g.) separated. These sintered at 205° and melted at 210° with darkening and subsequent loss of gas. They were probably 4:5-*dicarboxy-1-naphthoylformic acid* (Found: C, 58·15; H, 2·7. $C_{14}H_8O_7$ requires C, 58·3; H, 2·8%). If isolated by concentration and cooling of the acidified solution, the acid, on crystallisation from acetic anhydride–acetic acid, was obtained as a yellow powder, m. p. 202—204° (decomp.) This was probably the *anhydride* of 4:5-dicarboxy-1-naphthoylformic acid (Found: C, 61·9; H, 2·3. $C_{14}H_6O_6$ requires C, 62·2; H, 2·2%).

The oxidation was repeated using more potassium permanganate (1·6 g.) and refluxing the mixture for 1·5 hours. Crystallisation of the resulting product (0·1 g.) from acetic anhydride–acetic acid yielded fine, colourless needles, m. p. 274—275°, of 4-carboxynaphthalic anhydride (Found: C, 64·7; H, 2·4. Calc. for $C_{13}H_6O_4$: C, 64·5; H, 2·5%).

(b) *With nitric acid.* 4-Acetylnaphthalic anhydride (0·9 g.) was heated with concentrated nitric acid (4 c.c.) and water (2 c.c.) for 6 hours at 180—200° and then for 2 hours at 230—240°. Evaporation of the resulting solution yielded a white powder (0·5 g.), which on crystallisation from a small volume of dilute hydrochloric acid gave a solid, m. p. 233° (with loss of water), which was dried *in vacuo* over phosphoric oxide and sodium hydroxide (Found: C, 46·9; H, 2·4. Calc. for $C_{16}H_8O_8$: C, 47·25; H, 2·4%). An aqueous solution of the acid did not give a precipitate with aqueous barium chloride. The tetramethyl ester, m. p. 128—129°, was prepared by using diazomethane. The acid was therefore benzene-1:2:3:4-tetracarboxylic acid (*cf.* Hamford and Simonsen, *J.*, 1910, **97**, 1904; Fieser and Peters, *loc. cit.*).

3-Ethylacenaphthene (*cf.* Fleischer and Wolff, *loc. cit.*).—3-Acetylacenaphthene (31 g.) in toluene (300 c.c.) was added to a mixture of amalgamated zinc (from 150 g. of zinc), concentrated hydrochloric acid (400 c.c.), and water (100 c.c.). The mixture was stirred at the boil for 3 hours, more hydrochloric acid (200 c.c.) being then added. After a further 3 hours, the toluene layer was washed with water and dried, and the toluene removed. The residue was distilled and the fraction, b. p. 290—305°/763 mm., collected. The 3-ethylacenaphthene was an almost colourless oil, partly solidifying at room temperature. The solid portion, after 3 recrystallisations from methyl alcohol, separated in colourless plates, m. p. 41·5—42·5°. Fleischer and Wolff recorded m. p. 42·5—43°. The *picrate* crystallised from the minimum

of dry alcohol in red needles, m. p. 91—92° (Found: C, 58·2; H, 4·1; N, 9·8. $C_{14}H_{11}C_6H_3O_7N_3$ requires C, 58·4; H, 4·1; N, 10·2%).

4-Ethylnaphthalic Anhydride.—To a solution of crude 3-ethylacenaphthene (4 g.) in boiling acetic acid (150 c.c.) was added sodium dichromate (20 g.) in small portions and the whole was refluxed for 2 hours. It was poured into ice–water and later the precipitate was collected and extracted with 5% aqueous sodium carbonate (200 c.c.). The extract was acidified and the solid (2·3 g., 43%) crystallised 3 times from acetic acid to give colourless needles, m. p. 164—164·5°, of *4-ethylnaphthalic anhydride* (Found: C, 74·0; H, 4·3. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%).

The anhydride was oxidised to 4-carboxynaphthalic anhydride, m. p. 273—274°, by means of potassium permanganate.

The *imide* was obtained in almost colourless plates and needles, m. p. 195—196°, from alcohol (Found: C, 74·3; H, 5·1; N, 6·2. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The *N-methylimide* separated from alcohol in colourless rosettes, m. p. 140° (Found: C, 75·3; H, 5·7; N, 6·1. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%).

3′ (or 4′)-Ethyl-1 : 7′-thionaphthenacenaphthenylindigo.—Oxidation of 3-ethylacenaphthene in acetic acid solution by sodium dichromate (insufficient for complete conversion into 4-ethylnaphthalic anhydride) produced a mixture from which some anhydride could be extracted with aqueous sodium carbonate. After repeated extractions, the residue was digested with aqueous sodium hydrogen sulphite and filtered and the filtrate acidified. On boiling of the mixture, the yellow precipitate thickened and was filtered off. After repeated crystallisation from alcohol, yellow needles, m. p. 117—119°, of impure 3-ethylacenaphthenequinone (Found: C, 78·65; H, 4·8. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%) were obtained.

A hot solution of the quinone in acetic acid was mixed with a hot solution of 2-hydroxythionaphthen in the same solvent, a little hydrochloric acid was added, and the mixture boiled. On cooling, a red precipitate was formed and did not redissolve on boiling. It crystallised from acetic acid in bright red globules of microcrystalline needles, m. p. 216—217°, of *3′(or 4′)-ethyl-1 : 7′-thionaphthenacenaphthenylindigo* (Found: S, 9·9. $C_{32}H_{18}O_4S$ requires S, 9·4%). The colour of a solution in sulphuric acid was green.

2-Ethylacenaphthene (method: Mayer and Kaufmann, *loc. cit.*).—A 23% yield of a yellowish oil, b. p. 145—150°/4 mm., was obtained. On cooling in liquid air, the oil set to a glass, which quickly liquefied at room temperature. Isomers may therefore be present, but none could be isolated. The picrate was obtained from the minimum of dry alcohol in orange-red rods, m. p. 101·5—102·5° (Found: C, 58·2; H, 4·2; N, 10·2. Calc. for $C_{14}H_{14}C_6H_3O_7N_3$: C, 58·4; H, 4·1; N, 10·2%). Mayer and Kaufmann recorded m. p. 95—96°. Admixture of 3-ethylacenaphthene picrate, m. p. 91—92°, depressed the melting point to below 78°.

3-Ethylnaphthalic Anhydride.—To a solution of 2-ethylacenaphthene (10 g.) in boiling acetic acid (300 c.c.) was added sodium dichromate (40 g.) in small portions, and the whole was refluxed for 6 hours and poured into ice–water. The solid was collected and extracted with 5% aqueous sodium carbonate, and the extract treated with charcoal, filtered, and acidified. The precipitate was crystallised from acetic acid containing a little acetic anhydride to yield a colourless, crystalline solid (4·5 g., 36%), which was recrystallised 3 times from acetic acid, affording colourless needles, m. p. 192—193° (softening at 189°) of 3-ethylnaphthalic anhydride (Found: C, 74·15; H, 4·4. Calc. for $C_{14}H_{10}O_3$: C, 74·3; H, 4·4%). Mayer and Kaufmann recorded m. p. 180°. Admixture of 4-ethylnaphthalic anhydride, m. p. 164—164·5°, depressed the m. p. to 141—144°. Fractional crystallisation of the residues yielded no other homogeneous product.

The *imide* was obtained in colourless rhombohedra, m. p. 217—218·5°, from alcohol (Found: C, 74·6; H, 5·25; N, 5·9. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The *N-methylimide* crystallised from alcohol in colourless, prismatic needles, m. p. 113—114° (Found: C, 75·0; H, 5·1; N, 5·95. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%).

2-Ethylacenaphthenequinone.—Sodium dichromate (18 g.) was added all at once to a solution of 2-ethylacenaphthene (5·5 g.) in boiling acetic acid (250 c.c.), and after the violent reaction had subsided the whole was refluxed for 30 minutes. It was poured into ice–water, and the precipitate was repeatedly extracted with 5% aqueous sodium carbonate. The extracts were treated with charcoal and acidified, yielding 3-ethylnaphthalic anhydride (1 g.). The residual, tarry mass was extracted with sodium hydrogen sulphite solution, and the extract treated with charcoal, filtered, acidified, and boiled. The yellow precipitate was treated with 5% aqueous sodium carbonate to remove the last traces of anhydride which adhere very tenaciously, and the residue was crystallised 4 times from alcohol to give yellow needles, m. p. 150—152°, of *2-ethylacenaphthenequinone* (Found: C, 79·6; H, 5·2. $C_{14}H_{12}O_2$ requires C, 80·0; H, 4·8%).

2′(or 5′)-Ethyl-1 : 7′-thionaphthenacenaphthenylindigo.—This was prepared in the same way as its 3′(or 4′)-isomer, crystallisation from acetic acid yielding a brownish-red powder, m. p. 204—206° (Found: S, 9·0. $C_{32}H_{18}O_4S$ requires S, 9·4%). The colour of a solution in sulphuric acid was green, that of its isomer being slightly yellower. A mixture of the two *dyes* melted below 180°.

Oxidation of 3-Ethylnaphthalic Anhydride.—(a) *With potassium permanganate.* 3-Ethylnaphthalic anhydride (0·4 g.) was dissolved in 5% aqueous sodium hydroxide (50 c.c.) and to the cold solution was added a solution of potassium permanganate (1·7 g.) in water (30 c.c.). After 3 days at room temperature a little alcohol was added and the mixture warmed to destroy any excess of permanganate. Filtration, acidification, and cooling yielded a precipitate, which crystallised from acetic acid containing a little acetic anhydride in almost colourless rosettes, m. p. 280—290° (softening at 283°), of *3-carboxynaphthalic anhydride* (Found: C, 64·1; H, 2·65. $C_{13}H_6O_6$ requires C, 64·5; H, 2·5%). Admixture of 4-carboxy-

naphthalic anhydride, m. p. 274—275°, depressed the m. p. to 257—259°. The *methyl* ester, prepared by using diazomethane, was crystallised from acetic acid in irregular masses, m. p. 226—227° (Found: C, 65·15; H, 3·3. $C_{14}H_8O_5$ requires C, 65·6; H, 3·1%). Fieser and Peters (*loc. cit.*) gave m. p. 222° for the methyl ester of 4-carboxynaphthalic anhydride, and Fieser and Cason (*loc. cit.*) recorded m. p. 191—192° for the 2-isomer.

(b) ***With nitric acid.*** 3-Ethylnaphthalic anhydride was oxidised under various conditions with nitric acid and water in a sealed tube. Only an unidentified acid, a white powder, m. p. 236—240° (decomp.) (Found: C, 44·7, 44·7; H, 2·5, 2·3%), could be isolated. With diazomethane, this acid yielded a polymethyl ester as colourless plates, m. p. 139—141° (Found: C, 49·2, 49·0; H, 3·9, 3·9%). An aqueous solution of the acid gave on the addition of a solution of barium chloride clusters of needles. Nitric acid oxidation of 3-ethylnaphthalic anhydride would not yield a benzenetetracarboxylic acid, probably because the ring carrying the ethyl group was attacked first. It should be noted that 3-*tert.*-butylnaphthalic anhydride in a similar reaction could only be converted into an impure benzene-1 : 2 : 3 : 5-tetracarboxylic acid, whereas 2 : 5-di-*tert.*-butylnaphthalic anhydride yielded that acid without any difficulty (*cf.* Part III).

Action of Aluminium Chloride on 3-Ethylacenaphthene.—3-Ethylacenaphthene (5 g.) in carbon disulphide (50 c.c.) was refluxed with anhydrous aluminium chloride (4 g.) for 4 hours. A tarry mass was formed, but little hydrogen chloride was evolved. After careful decomposition with water, the carbon disulphide layer was separated and dried, and the solvent removed. The residue was distilled and all the high-boiling material collected. The oil, somewhat discoloured, was oxidised in refluxing acetic acid (50 c.c.) by sodium dichromate (8 g.) for 2 hours, the whole being then poured into ice–water. The precipitate was extracted with 5% aqueous sodium carbonate. The extract was acidified and filtered immediately. On storage, more precipitate formed in the filtrate, and was collected and crystallised 3 times from acetic acid, then having m. p. 267·5—269°, not depressed on admixture of authentic naphthalic anhydride. The first precipitate contained tarry, semi-solid material, which could be separately crystallised. After 3 recrystallisations from acetic acid, it melted at 187°. This m. p. was not depressed on admixture of authentic 3-ethylnaphthalic anhydride, m. p. 192—193°, but was depressed to 132—137° on admixture of 4-ethylnaphthalic anhydride, m. p. 164—164·5°. From the remaining precipitated material no homogeneous product could be obtained.

In another experiment, only naphthalic anhydride and 4-ethylnaphthalic anhydride (from unchanged 3-ethylacenaphthene), but no 3-ethylnaphthalic anhydride, were isolated.

It can therefore be stated that 3-ethylacenaphthene was partly dealkylated to acenaphthene under the influence of aluminium chloride, and some 2-ethylacenaphthene may be formed under the same conditions. The investigation is being continued.

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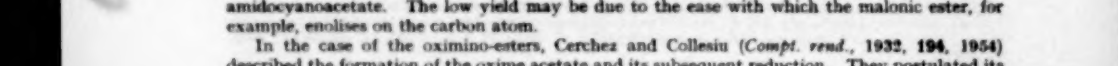
490. *The Reductive Acetylation of Aliphatic Nitro-compounds.*

By CHARLES SIMONS.

The reductive acetylation of ethyl nitromalonate and ethyl nitrocyanoacetate has been effected in low yield. This may throw some light on the enolisation of nitromalonic esters.

THE reductive acetylation of aromatic nitro-compounds is known (*e.g.*, Kohn and Krasso, *J. Org. Chem.*, 1948, **13**, 329) and also that of aliphatic oximino-compounds (B.P. 583,307). Ethyl nitromalonate and ethyl nitrocyanoacetate have been successfully reduced in this laboratory in 30% yield by zinc, acetic acid, and acetic anhydride to ethyl acetamidomalonate and acetamidocyanoacetate. The low yield may be due to the ease with which the malonic ester, for example, enolises on the carbon atom.

In the case of the oximino-esters, Cerchez and Collesiu (*Compt. rend.*, 1932, **194**, 1954) described the formation of the oxime acetate and its subsequent reduction. They postulated its existence in two forms (III and IV):

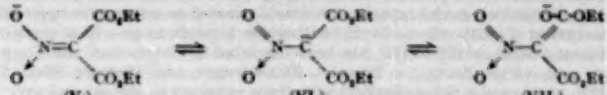


(I.) (II.) (III.) (IV.)

The existence of (IV) or an analogue would seem to be essential for reduction to ethyl acetamidomalonate.

If nitromalonic ester (VI) may be compared with *o*-nitrophenol, enolisation would afford the

aci-nitro-compound (V). It can also be substituted in sodium ethoxide solution (cf. Weisblat and Lyttle, *J. Amer. Chem. Soc.*, 1949, **71**, 3079) and this probably proceeds through (VII).



(V.) (VI.) (VII.)

[Where (V)—(VII) are some of the canonical forms of the resonating enol ion.]

Thus nitromalonic ester might exist mainly in form (VII). This aspect was discussed by Arndt and Rose (*J.*, 1935, 7). Meyer (*Ber.*, 1914, **47**, 2380) suggested that with compounds of the type $R{\cdot}CO{\cdot}CH_2{\cdot}NO_2$ enolisation is on the carbon and not on the nitrogen atom; this was supported by Kuhn and Albrecht (*Ber.*, 1927, **60**, 1297). Arndt and Rose, disputing this, based their conclusions on esterification of the nitronic acid with diazomethane and claimed nitronic esters of type (V); they disagreed with the conclusions of Steinkopf (*Annalen*, 1923, **434**, 29), who claimed the preparation of nitronic esters from methyl iodide and the silver salt. It must be noted that the properties of these esters differed.

Weisblat and Lyttle (*loc. cit.*) prepared ethyl α-nitro-α-carbethoxy-β-3-indolylpropionate from ethyl nitromalonate and gramine, but reduction with zinc and acetic acid only gave 56% of ethyl α-hydroxylamino-β-3-indolylpropionate.

One possible explanation of the fact that nitromalonic ester is reduced under the conditions described below only to about one-third of the extent that oximinomalonic ester is reduced may be that steps corresponding to (III)—(IV) are lacking, owing to enolisation on the carbon and not on the nitrogen atom.

Experimental.

Ethyl Acetamidocyanoacetate.—Ethyl nitrocyanoacetate (Conrad and Schulze, *Ber.*, 1909, **42**, 740) (10 g.), acetic acid (40 ml.), acetic anhydride (40 ml.), and a trace of copper powder were mechanically stirred at 50° with addition of zinc dust. The rate of addition was decreased and the temperature allowed to rise to 80° and kept there until 25 g. of zinc had been added. The mixture was cooled, filtered, and washed with acetic acid. The filtrates were evaporated in a vacuum and the syrup was diluted with water. Crystals (3 g.) were deposited, having m. p. 131—134° alone or mixed with an authentic sample (Found: N, 15·7; Ac, 25·7. Calc. for $C_7H_{10}O_3N_2$: N, 16·5; Ac, 25·3%).

Ethyl Acetamidomalonate.—Ethyl nitromalonate (Wahl, *Bull. Soc. chim.*, 1901, [iii], **25**, 926; Arndt and Rose, *loc. cit.*) was treated in an analogous fashion, affording a 30% yield of ethyl acetamidomalonate, m. p. and mixed m. p. 94° (Found: N, 6·4. Calc. for $C_7H_{11}O_5N$: N, 6·5%). The oil remaining after removal of the crystals was unchanged starting material.

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491. *Steroids and Related Compounds. Part X. The Preparation of Pregna-5 : 17-diene-3β : 21-diol.*

By D. Magrath, D. S. Morris, V. Petrow, and R. Rover.

The preparation of pregna-5 : 17-diene-3β : 21-diol (VI; R = H) from dehydro*epi*androsterone acetate (I) by two novel routes is reported.

Dehydration of methyl 3β-acetoxy-17β-hydroxy-17-*iso*pregn-5-en-21-oate (IV; R = Ac, R′ = Me) with anhydrous formic acid leads to an abnormal product to which the structure of a methyl 3β-acetoxy-17-methylnorpregna-5 : 13(12)-dien-21-oate (IX; R = Ac, R′ = Me) is tentatively proposed.

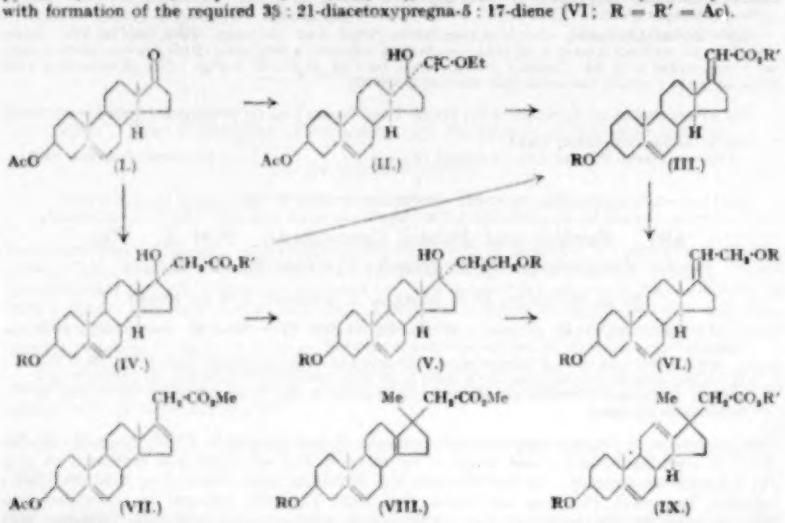
The conversion of dehydro*epi*androsterone acetate (I) into pregna-5 : 17(20)-diene-3β : 21-diol (VI; R = H) has hitherto been achieved by reaction with acetylene and reduction to give 17α-vinylandrost-5-ene-3β : 17β-diol (Ruzicka and Hofmann, *Helv. Chim. Acta*, 1937, **20**, 1280); Inhoffen, Logemann, Hohlweg, and Serini, *Ber.*, 1938, **71**, 1024), followed by conversion into (VI; R = H) by treatment with (*a*) trichloroacetic acid in acetic anhydride (Miescher and Scholz, *Helv. Chim. Acta*, 1939, **22**, 120) or (*b*) phosphorus tribromide and then potassium acetate (Ruzicka and Müller, *ibid.*, p. 416). Both routes prove satisfactory with small quantities of

materials, but the experimental conditions required for optimum yields are rather critical and thus limit the value of the methods for large-scale working. As substantial quantities of (VI) were required for studies of methods of building up the ketol side chain present in the glucocorticoids (*e.g.*, Cortisone), model experiments were instituted on alternative approaches.

Condensation of (I) with ethoxyethynylmagnesium bromide to give 3β-acetoxy-17α-ethoxyethynyl-17-*iso*androst-5-en-17β-ol (II) has been described by Arens and van Dorp (Dutch P. 63,015/1949) and independently by Heusser, Eichenberger, and Plattner (*Helv. Chim. Acta*, 1950, **33**, 370), their results being identical with those obtained in this laboratory. In analogy with observations reported by Heilbron, Jones, Julian, and Weedon (*J.*, 1949, 1823) in the vitamin A field, we now find that (II) undergoes ready conversion into ethyl 3β-acetoxy-*iso*pregna-5 : 17-dien-21-oate (III; R = Ac; R′ = Et) when heated with ethanolic sulphuric acid for two minutes on the water-bath. Alkaline hydrolysis of this product furnished 3β-hydroxypregna-5 : 17-dien-21-oic acid (III; R = R′ = H), identical with the acid described by Plattner and Schreck (*Helv. Chim. Acta*, 1939, **22**, 1178). Reduction of the acid, or of its ethyl ester, with lithium aluminium hydride (cf. Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197) led to the formation of the required diol (VI; R = H).

Ethyl 3β-acetoxy-17β-hydroxy-17-*iso*pregn-5-en-21-oate (IV; R = Ac, R′ = Et) formed the starting point of a second novel approach to pregna-5 : 17-diene-3β : 21-diol (VI; R = R′ = H). The latter could clearly be obtained from (IV) by reduction and dehydration, which could presumably be carried out in either order. In practice, however, reduction followed by dehydration was preferable.

Preparation of compounds of type (IV) has been described by Reichstein, Müller, Meystre, and Sutter (*Helv. Chim. Acta*, 1939, **22**, 741) who condensed (I) with ethyl bromoacetate under Reformatsky conditions, but failed to isolate (IV; R = Ac, R′ = Et). Alkaline hydrolysis of the product furnished the crystalline acid (IV; R = R′ = H), converted into (IV; R = Ac, R′ = Me), from which, by Bouveault–Blanc reduction, they obtained (V; R = H) in low overall yield. We now find, in contrast, that direct crystallisation of the crude Reformatsky product readily yields the hitherto undescribed ethyl ester (IV; R = Ac, R′ = Et), which is converted into 17-*iso*pregn-5-ene-3β : 17β : 21-triol (V; R = H) by lithium aluminium hydride in yields exceeding 80%. Diacetylation of the triol, followed by treatment with thionyl chloride in pyridine (cf. Darzens, *Compt. rend.*, 1911, **152**, 601), resulted in the desired exocyclic dehydration with formation of the required 3β : 21-diacetoxypregna-5 : 17-diene (VI; R = R′ = Ac).



Dehydration of (IV) to (III), followed by reduction with lithium aluminium hydride, proved a less successful approach to (VI) owing to unexpected difficulties in achieving dehydration of

the 17β-hydroxyl grouping present in (IV). Methods such as reaction with thionyl chloride or phosphorus pentachloride in benzene, or distillation over anhydrous copper sulphate under reduced pressure, reported by Reichstein *et al.* (*loc. cit.*), proved incapable of consistent repetition. Similar results were obtained on employing the distillation procedure of Plattner and Schreck (*loc. cit.*), although in this case a 50% yield of (III; R = Ac, R′ = Me) was obtained in one instance. In general, however, the distillation products contained substantial quantities of (I).

Attempts to enforce dehydration of (IV; R = Ac, R′ = Me) with anhydrous formic acid under reflux were accompanied by marked colour changes of the solution which rapidly became an intense violet-blue. Termination of the experiment at this stage led to a new unsaturated acetoxy-ester (*A*) isomeric with methyl 3β-acetoxypregna-5 : 17-dien-21-oate (VI; R = Ac, R′ = Me). Its formulation as the Δ^{16}-dehydration product (VII) was rendered improbable by catalytic hydrogenation studies when two molecules of hydrogen were absorbed to give a tetrahydro-derivative not identical with methyl 3β-acetoxy*allo*pregnan-21-oate (Plattner and Schreck, *loc. cit.*). This observation, together with the formation of the intense purple-blue coloration during its formation (see above), led to the conclusion that dehydration had been accompanied by structural changes of a more profound character. Accordingly we propose the constitution of a methyl 3β-acetoxy-17-methylnorpregna-5 : 13(12)-dien-21-oate (IX; R = Ac, R′ = Me) for compound (*A*) on the basis of the following evidence : (*a*) 17α-hydroxyandrostane undergoes retropinacolinic rearrangement to ψ-androstene when heated with formic acid, the boiling solution likewise becoming deep violet (Miescher and Kägi, *Helv. Chim. Acta*, 1939, **22**, 761); (*b*) both ψ-androstene and compound (*A*) give intense blue-violet colours on treatment of their solutions in sulphuric acid–acetic acid with bromine–acetic acid (Miescher and Kägi, *loc. cit.*; see also Kägi and Miescher, *ibid.*, p. 683); and (*c*) the formulation of ψ-androstene as a retropinacolinic dehydration product is supported by chemical evidence (Miescher and Kägi, *loc. cit.*). A $\Delta^{13(17)}$-structure is, of course, not possible in our case and, as compound (*A*) fails to give a blue nitrosochloride in the Thiele test (*Ber.*, 1894, **27**, 454) in contrast to ψ-androstene, we prefer to assign it structure (IX) rather than the isomeric structure (VIII).

Experimental.

M. p.s are uncorr. Microanalyses are by Drs. Weiler and Strauss, Oxford. Optical rotations were measured in chloroform solution in a 2-dm. tube unless stated otherwise.

Ethyl 3β-Acetoxypregna-5 : 17-dien-21-oate (III; R = Ac, R′ = Et).—3β-Acetoxy-17α-ethoxyethynylandrost-5-en-17β-ol (400 mg.; m. p. 140—141°) dissolved in ethanol (8 ml.) was treated with 3N-sulphuric acid (2 ml.), and the mixture heated on the steam-bath for 2 minutes. After the mixture had been poured into water the precipitated solids were collected, dried over potassium hydroxide, and crystallised from aqueous ethanol, giving *ethyl 3β-acetoxypregna-5 : 17-dien-21-oate* (55%), leaflets, m. p. 117°, $[\alpha]_D^{20}$ −69·8° (*c*, 0·394) (Found : C, 74·5; H, 8·8. $C_{25}H_{36}O_4$ requires C, 75·0; H, 9·1%).

3β-Hydroxypregna-5 : 17-dien-21-oic Acid (III; R = R′ = H).—The foregoing ester (500 mg.) was heated under reflux with methanolic sodium hydroxide (10 ml. of 2N.) for 1½ hours, after which the solution was poured into water (50 ml.). The mixture was boiled for 10 minutes and then acidified with hydrochloric acid until acid to Congo-red. The precipitated acid was collected, purified through the sodium salt, and finally crystallised from methanol. 3β-Hydroxypregna-5 : 17-dien-21-oic acid formed small crystals (37%), m. p. 245° (Found : C, 76·0; H, 9·1. Calc. for $C_{21}H_{30}O_3$: C, 76·3; H, 9·2%). Plattner and Schreck (*loc. cit.*) give m. p. 249—250° (corr.); Marker *et al.* (*J. Amer. Chem. Soc.*, 1942, **64**, 1276) give m. p. 252—253°.

Pregna-5 : 17-diene-3β : 21-diol (VI; R = H).—The ester (III; R = Ac, R′ = Et) (170 mg.) in dry ether (10 ml.) was added to a solution of lithium aluminium hydride in dry ether (50 ml. of 0·2%), and the mixture heated under reflux for 15 minutes. Water was then carefully added followed by 3N-sulphuric acid, until the solution was acid to Congo-red. The ethereal layer was washed until neutral and dried ($MgSO_4$), and the ether removed. Crystallisation of the residue from methanol gave pregna-5 : 17-diene-3β : 21-diol (93%), as colourless leaflets, m. p. 191—192°, $[\alpha]_D^{20}$ −57·6° (*c*, 0·544 in ethanol) (Found : C, 80·1; H, 10·1. Calc. for $C_{21}H_{32}O_2$: C, 79·7; H, 10·2%). Miescher and Scholz (*loc. cit.*) give m. p. 198°; Ruzicka and Müller (*loc. cit.*) give m. p. 199—199° (corr.), $[\alpha]_D$ −59·5° ±1·5° (in ethanol).

Ethyl 3β-Acetoxy-17β-hydroxy-17-iso-pregn-5-en-21-oate (IV; R = Ac, R′ = Et).—Ethyl bromoacetate (10 g.) was added as quickly as reaction permitted to a stirred mixture of dehydroepiandrosterone acetate (20 g.), dry benzene (168 ml.), activated zinc (23·5 g.), and a crystal of iodine. The mixture was then heated on a steam-bath for 1½ hours, after which it was cooled in ice and the magnesium complex decomposed by the addition of 2N-hydrochloric acid (200 ml.). The product, extracted with ether ("crude Reformatsky product," see below), was taken up in methanol. *Ethyl 3β-acetoxy-17β-hydroxy-17-iso-pregn-5-en-21-oate* separated slowly and, after crystallisation from methanol, formed needles, m. p. 112—113°, $[\alpha]_D^{20}$ −74·0° (*c*, 0·905) (Found : C, 71·1; H, 8·9. $C_{25}H_{38}O_4$ requires C, 71·7; H, 9·2%).

17-iso-Pregn-5-ene-3β : 17β : 21-triol (V; R = H).—The foregoing ester (500 mg.) in dry ether (20 ml.) was added slowly with shaking to a solution of lithium aluminium hydride in ether (50 ml. of 0·6%). The

mixture was heated under reflux for 15 minutes, cooled, decomposed with ice, and shaken vigorously with 5*N*-hydrochloric acid (20 ml.). The white solid which separated was collected and united with the crystals which separated on concentration of the ethereal layer. Purification from ethanol yielded 17-*iso*pregn-5-ene-3β : 17β : 21-triol (82%) as glittering plates, m. p. 235—239° (Found : C, 75·0; H, 10·25. Calc. for $C_{21}H_{34}O_3$: C, 75·4; H, 10·25%). Similar results were obtained on using the "crude Reformatsky product." Reichstein *et al.* (*loc. cit.*) give m. p. 243—245° (corr.).

Acetylation of the triol gave the diacetate, m. p. 156—157°, $[\alpha]_D^{20}$ −59·8° (*c*, 0·413 in acetone). Reichstein *et al.* (*loc. cit.*) give m. p. 159—160° (corr.), $[\alpha]_D^{20}$ −65·3° ± 1·5° (in acetone).

3β : 21-*Diacetoxypregna*-5 : 17-*diene* (VI; R = Ac).—The foregoing diacetate (2·0 g.) in dry pyridine (10 ml.) was treated at 0° with thionyl chloride (0·44 ml.) added dropwise with shaking. The mixture was then poured into ice-water (50 ml.), and the precipitated gummy solids were thoroughly ground. After 2 hours the product was collected, dried over potassium hydroxide, and crystallised from ethanol, giving 3β : 21-diacetoxypregna-5 : 17-diene, colourless crystals, m. p. 135°, $[\alpha]_D^{20}$ −47·1° (*c*, 0·530). Miescher and Scholz (*loc. cit.*) give m. p. 136·5—137°. Ruzicka and Müller (*loc. cit.*) give m. p. 135—136° (corr.). Hydrolysis gave pregna-5 : 17-diene-3β : 21-diol, m. p. 194—196°, $[\alpha]_D^{20}$ −58·2° (*c*, 0·860 in ethanol) (Found : C, 79·1; H, 10·2. Calc. for $C_{21}H_{32}O_2$: C, 79·7; H, 10·2%), not depressed on admixture with the product prepared by the ethoxyacetylene route.

Preparation of Pregna-5 : 17-*diene*-3β : 21-*diol from Methyl* 3β-*Acetoxy*-17β-*hydroxy*-17-*iso*pregn-5-*en*-21-*oate*.—Hydrolysis of the "crude Reformatsky product" (10 g.) gave 3β : 17β-dihydroxy-17-*iso*pregn-5-en-21-oic acid (7·6 g.; m. p. 235°), converted into (IV; R = H, R′ = Me) (83%), m. p. 158°, by the method of Plattner and Schreck (*loc. cit.*). Dehydration of the ester by vacuum-distillation as described by Plattner and Schreck (*loc. cit.*) gave (III; R = Ac, R′ = Me) in poor yield, reduced to (VI; R = H) (91%), m. p. 194—198°, $[\alpha]_D^{20}$ −60·1° (*c*, 0·616 in ethanol) by lithium aluminium hydride. Dehydration by thionyl chloride or phosphoric oxide in benzene (Reichstein *et al.*, *loc. cit.*) likewise gave (III; R = Ac, R′ = Me) in poor yield, reduced to (VI; R = H).

Methyl 3β-*Acetoxy*-17-*methylisopregna*-5 : 13(12)-*dien*-21-*oate* (IX; R = Ac, R′ = Me).—The ester (IV; R = Ac, R′ = Me) (1·0 g.) in formic acid (5 ml. of 98%) was heated on the steam-bath for 5 minutes, the colour changing from yellow to violet-blue. The mixture was poured into water, and the product extracted with ether and crystallised from ethanol. *Methyl* 3β-*acetoxy*-17-*methylisopregna*-5 : 13(12)-*dien*-21-*oate* formed colourless leaflets (50%), m. p. 101° (Found : C, 74·2; H, 9·0. $C_{24}H_{36}O_4$ requires C, 74·6, H, 9·8%). Hydrolysis furnished the *hydroxy-acid* (IX; R = R′ = H) which, purified from acetone–light petroleum, had m. p. 163—165° (Found : C, 76·2, H, 9·0. $C_{21}H_{32}O_3$ requires C, 76·3; H, 9·2%).

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492. *The Seed Fat of* Macadamia ternifolia.

By R. E. Bridge and T. P. Hilditch.

The nuts of *Macadamia ternifolia*, a tree found in South Queensland and elsewhere in Australia, contain seeds with a high content of a fatty oil resembling olive oil in general character. Its component acids, however, are made up of oleic (60%) and hexadec-9-enoic • (palmitoleic) acid (20%) with about 8% of palmitic, 3% of stearic, and very small proportions of linoleic, eicosenoic, myristic, and arachidic acids. So large a proportion of hexadecenoic acid in the seed fat of a terrestrial plant has not been observed previously, and further studies of the seed fats of related genera would be of value.

The evergreen tree *Macadamia ternifolia*, belonging to the family Proteaceæ, grows between the latitudes of 25° and 32° S. in Eastern Australia (northern New South Wales and southern Queensland) and attains about 60 feet in height. It is cultivated to a considerable extent in these areas and also in Hawaii and California. It bears hard woody nuts (termed in Australia Queensland nuts or Australian Bush nuts) which contain a single seed. According to Lathrop (*J. Oil Fat Ind.*, 1925, **2**, 44) Hawaii nuts of this species consist of shell 70% and kernel 30%, whilst Morrison (*J. Sydney Tech. Coll. Chem. Soc.*, 1922, **1**, 84) reported that Australian kernels yielded 73% of a liquid fatty oil (iodine value 74·5—75·8, saponification equivalent 287) which consisted mainly of glycerides of oleic acid, accompanied by small proportions of palmitic and stearic acids, and thus closely resembled the best quality of olive oil.

• Geneva numbering.

Some time ago Dr. J. R. Vickery, Chief of the Division of Food Preservation, Australian Commonwealth Scientific and Industrial Research Organisation, sent us a small specimen of Macadamia oil, the detailed composition of which we have determined. The analytical characteristics of this oil were very close to those given by the earlier observers (*loc. cit.*), namely, iodine value 74·8, saponification equivalent 292·0, free fatty acid (as oleic) 0·5%, with 1·0% of unsaponifiable matter. When, however, the mixed fatty acids of the oil were determined in detail by separating them by crystallisation from acetone and then from ether at low temperatures into four groups of differing unsaturation, followed by fractional distillation of the methyl esters of each of the four groups of acids, it became evident that a considerable amount of monoethenoid acid other than oleic accompanied the latter. The acid in question was shown to be hexadec-9-enoic • (palmitoleic) acid, present in traces in many, probably all, seed fats (Hilditch and Thompson, *J. Soc. Chem. Ind.*, 1937, **56**, 434T; Hilditch and Jasperson, *ibid.*, 1938, **57**, 84; 1939, **58**, 187), but not hitherto observed in major proportions in any seed fat.

Our detailed examination of the mixed fatty acids of the *Macadamia ternifolia* oil led to the following composition: myristic 1·6, palmitic 8·0, stearic 3·3, arachidic 2·2, behenic 0·8, hexadecenoic 20·4, oleic 59·3, linoleic 2·2, and eicosenoic 2·2% (wt.). Macadamia oil is thus distinguished by its very low content of diethenoid (linoleic) acid, by the presence of a very small proportion of, apparently, an eicosenoic acid $C_{20}H_{38}O_2$, and, above all, by its content of 20% of the monoethenoid acid of the C_{16} series. The total amount and the relative proportions of saturated acids in the oil (with palmitic acid predominating) are similar to those in many other liquid seed oils of comparable general unsaturation (the minor proportions of myristic, arachidic, and behenic acids, it may be pointed out, are deduced from the ester-fractionation data, but the amounts present were too small to permit of definite identification as individual acids).

The seemingly exceptional occurrence of so great a proportion of hexadecenoic acid in this seed fat merits some consideration. This acid is present in similar proportions, but is accompanied by equally marked proportions of highly-unsaturated acids containing 20 and 22 carbon atoms in the molecule, in the fats of vegetable plankton and other marine flora (Lovern, *Biochem. J.*, 1936, **30**, 387; Hilditch, "Chemical Constitution of Natural Fats," 2nd Edn., 1947, pp. 24—26). It has also been observed in quantity in fats of some lower forms of land flora, such as those of diphtheria bacilli (Chargaff, *Z. physiol. Chem.*, 1933, **218**, 223), yeast (Newman and Anderson, *J. Biol. Chem.*, 1933, **102**, 219), or lycopodium spores (Riebsomer and Johnson, *J. Amer. Chem. Soc.*, 1933, **55**, 3352). The botanical family Proteaceæ, in which *Macadamia* is placed, includes over 900 species: of these about two-thirds are indigenous to Australia, whilst the remainder are natives of Cape Colony and the adjacent parts of South Africa. The members of this family are thought to be survivors from one of the more primitive types characteristic of the original flora of the Australian continent. It is conceivable that plants of such origin should elaborate seed fats differing in some respects from those of other plants. Again, many members of the Proteaceæ are xerophytic in character and habituated to arid conditions of growth (although this probably does not hold entirely in the case of *Macadamia*); seed fats of such species have not, however, yet been studied in detail.

Rather, therefore, than regarding the presence of hexadecenoic acid in quantity in *Macadamia ternifolia* seed fat as a completely abnormal feature in a terrestrial seed fat, we prefer merely to record our findings and to suggest that further study of seed fats, of other species of Proteaceæ, of other species of the elemental Australasian flora, or of other xerophytic species, would be of great interest and might reveal further specific relations between seed-fat composition and the biological development of plant species.

Experimental.

Determination of the Component Acids of Macadamia ternifolia *Seed Fat.*—The mixed acids (93·2 g.) obtained by hydrolysis of 100 g. of the fat were crystallised, first from 10% solution in acetone at −50°. The acids left in solution were then crystallised from acetone at −60°, most of the polyethenoid acid present being left in solution (*D*), and the acids (*C*) deposited at −60° consisting mainly of monoethenoid compounds. The acids deposited from acetone at −50° were further crystallised from 10% solution in ether at −40°, the material deposited consisting almost wholly of saturated acids. The following groups of acids were thus obtained:

	Wt. (g.).	%.	Iodine value.
A, Insoluble in ether at −40°	13·7	14·7	8·0
B, Soluble in ether at −40°	50·8	54·5	87·9
C, Insoluble in acetone at −60°	20·1	21·6	94·5
D, Soluble in acetone at −60°	8·6	9·2	109·3

Each group of acids was separately converted into methyl esters, which were distilled in a vacuum through an electrically-heated and packed column. Table I shows the distilled fractions obtained from each group, with the temperature at the head of the column, and the equivalent and iodine value of each ester fraction.

The values in Table I clearly indicate the presence of hexadecenoic esters (methyl hexadecenoate, equiv. 268, iodine value 94·8) in quantity in the ester fractions *B*2, *B*3, C2, *C*3, *C*4, and *D*2. The residual fractions from esters *B*, *C*, and *D* evidently contained, in addition to unsaturated esters of the C_{18} series, a monoethenoid ester of an acid of higher carbon content; the amounts present were too small to permit its identification, and it has been calculated as methyl eicosenoate (equiv. 324, iodine value 78·4).

TABLE I.

Fractionation of methyl esters of fatty acids of groups A, B, C, *and* D.

Methyl esters from group *A*.

Fraction.	Wt. (g.).	Temp.	Sapon. equiv.	Iodine value.
1	1·08	120—135°	265·2	1·7
2	3·16	135—140	271·3	1·8
3	2·73	140—142	276·5	12·2
4	2·29	142—145	292·1	21·4
5	1·00	145—150	301·5	8·9
6	2·52	Residue	339·6 •	3·3 •
	12·78			

Methyl esters from group *B*.

Fraction.	Wt. (g.).	Temp.	Sapon. equiv.	Iodine value.
1	1·29	60—120°	257·3	55·5
2	1·89	120—135	267·4	79·4
3	2·57	140—145	271·4	79·7
4	2·21	,,	286·2	82·4
5	2·55	,,	291·8	84·5
6	2·58	,,	292·6	85·4
7	3·31	,,	293·8	85·4
8	4·92	,,	294·5	85·5
9	5·01	,,	294·8	85·4
10	3·98	,,	295·5	86·1
11	3·46	,,	295·8	85·5
12	3·45	,,	296·4	85·2
13	3·14	,,	295·7	85·9
14	3·64	,,	295·8	84·8
15	1·83	Residue	313·7 •	73·2
	45·83			

Methyl esters from group *C*.

Fraction.	Wt. (g.).	Temp.	Sapon. equiv.	Iodine value.
1	1·18	50—120°	257·2	61·5
2	1·54	120—135	268·1	91·9
3	3·07	135—140	268·7	93·8
4	2·55	,,	268·9	93·4
5	2·57	140	283·7	92·7
6	3·54	140—142	295·8	92·4
7	2·55	142—145	296·9	90·7
8	1·86	Residue	319·9 •	80·7 •
	18·86			

Methyl esters from group *D*.

Fraction.	Wt. (g.).	Temp.	Sapon. equiv.	Iodine value.
1	1·11	135—137°	260·1	83·2
2	1·89	137—138	267·5	93·3
3	1·98	140—145	279·2	109·5
4	1·66	,,	294·6	114·2
5	0·46	Residue	307·8 •	98·6 •
	7·10			

• Residual esters, freed from unsaponifiable matter:

*A*6 Sap. equiv. 332·4, iodine value 2·6. *C*8 Sap. equiv. 316·5, iodine value 79·3.
*B*15 ,, 307·1, ,, 72·6. *D*5 ,, 291·3, ,, 92·5.

The unsaturated C_{18} acids (which form the greater part of the oil) occurred to varying extents in all the separate groups, but those in groups *A* and *B* were wholly mono-ethenoid (methyl oleate, equiv. 296, iodine value 85·8). The polyethenoid C_{18} acids of the oil were concentrated in groups *C* and *D*, in representative C_{18} ester fractions of which the proportions of linoleic and oleic acids were determined spectrophotometrically after isomerisation with alkali at 180° for 1 hour as described by Hilditch, Morton, and Riley (*Analyst*, 1945, **70**, 68). The acids of ester fraction *D*4 were also isomerised with alkali at 170° for 15 minutes, but then gave negligible absorption at 268 mμ., indicating the absence of linolenic acid. The spectrophotometric data for the acids isomerised at 180° for 1 hour were:

	Mixed acids,		Composition of mixed acids (% wt.).	
Ester fraction.	Iodine value.	$E^{1\%}_{1cm}$ at 234 mμ.	Linoleic.	Oleic.
*C*8	97·0	66	7·3	92·7
*D*4	119·9	289	31·9	68·1

The components of each ester fraction were then calculated by procedures which have been described elsewhere in detail (Hilditch, *op. cit.*, pp. 505—509). The percentages of the component acids in each of the four groups, and therefrom those for the total fatty acids of the Macadamia oil, then follow (Table II).

TABLE II.

Component fatty acids of Macadamia oil.

Acid.	Acid groups. *A*. % (wt.).	*B*. % (wt.).	*C*. % (wt.).	*D*. % (wt.).	Total fatty acids (excluding unsaponifiable). % (wt.).	% (mol.).
Myristic	1·4	1·3	2·2	2·4	1·6	1·9
Palmitic	46·5	1·9	0·7	—	8·0	8·6
Stearic	21·9	0·2	—	—	3·3	3·2
Arachidic	14·9	—	—	—	2·2	1·9
as Behenic	5·5	—	—	—	0·8	0·6
Hexadecenoic	2·6	10·5	46·0	46·5	20·4	22·0
Oleic	6·8	85·4	39·8	33·3	59·3	57·7
Linoleic	—	—	3·3	16·3	2·2	2·0
as Eicosenoic	—	0·6	7·9	1·4	2·2	2·0
Unsaponifiable	0·4	0·1	0·1	0·1	—	—

Identification of Unsaturated Acids Present in Macadamia Oil.—Hexadecenoic, oleic and linoleic acids were identified in one or other of the ester fractions as follows :

Hexadecenoic acid. The acids (4·3 g.) from the mixed ester fractions *C*1, *C*2, *D*1, and *D*2 (equivalents 268 or below) were mixed and oxidised in acetone solution with powdered potassium permanganate (Armstrong and Hilditch, *J. Soc. Chem. Ind.*, 1925, **44**, 43T, 180T). After separation of the mono- and di-carboxylic acids produced, azelaic acid was isolated (m. p. 103—104°, unchanged on admixture with the pure acid; Found : equiv., 92·5. Calc. : equiv., 94·0). The monobasic acids (separated by distillation in steam) were recovered and fractionally distilled through a small column, giving fractions of acids with equivalents from 126 to 132 (heptoic acid, equiv. 130). The acid is thus hexadec-9-enoic acid.

Another portion of acids (3·0 g., from ester fraction *C*3) was oxidised in dilute aqueous alkaline solution at 0° with potassium permanganate (Lapworth and Mottram, *J.*, 1925, **127**, 1628), a dihydroxy-acid being formed which melted at 127—128° (unchanged on admixture with 9 : 10-dihydroxypalmitic acid).

Oleic acid. Acids (7·9 g.) from the mixed ester fractions *B*10—13 (equivalents 293·5—296·4) were oxidised as above in acetone solution with potassium permanganate. The dibasic acid product melted at 104—105° (unchanged on admixture with azelaic acid), and had an equivalent of 94·4. The monobasic acids produced were converted into ethyl esters and the latter fractionally distilled, fractions with equivalents from 178 to 185 being produced (ethyl nonoate, equiv. 186).

Another portion of the same acids (3·2 g.) was converted into the dihydroxy-acid by oxidation with dilute ice-cold alkaline permanganate, giving an acid of m. p. 130° (unchanged when mixed with 9 : 10-dihydroxystearic acid).

The octadecenoic acid present was thus ordinary oleic acid.

Linoleic acid. Acids (1·6 g.) from ester fraction *D*4 were dissolved in light petroleum (b. p. 40—60°), and bromine was added to the solution at 0°. A small deposit of crystalline bromo-addition product was produced, which after recrystallisation from the same solvent melted at 112° (unchanged when mixed with tetrabromostearic acid, m. p. 114°, from authentic linoleic acid).

We thank Dr. J. R. Vickery for his kindness in obtaining the specimen of Macadamia oil used in this work, and Professor D. A. Herbert of the University of Queensland who has supplied us with much botanical information on the genus *Macadamia*. We thank the Colonial Products Research Council for authority to publish these results, and for a grant to one of us (R. E. B.).

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493. *Kinetics and Mechanism of Aromatic Nitration. Part II. Nitration by the Nitronium Ion, NO_2^+, derived from Nitric Acid.*

By E. D. Hughes, C. K. Ingold, and R. I. Reed.

The plan underlying the investigation as developed in this collection of papers, which includes papers of several concurrent series, is explained. The series to which this paper belongs is concerned with the kinetics and products of aromatic nitration. The other series deal with various kinds of physical and synthetical evidence, all bearing directly or indirectly on the subject of nitration. In this paper the kinetics of aromatic nitration by nitric acid are considered. The treatment is divided into Sections, and the following summary of the paper is intended to render any of its Sections intelligible without the necessity of reading the others.

(1) *Kinetic Orders of Aromatic Nitration: The Nitronium Ion* (p. 2402).—Aromatic nitration displays second-order kinetics in sulphuric acid (Martinsen), and first-order kinetics in nitric acid; and in either nitromethane or acetic acid with nitric acid in constant excess, it exhibits zeroth-order kinetics for sufficiently reactive aromatic compounds, and first-order kinetics for sufficiently unreactive compounds. Nothing of special interest concerning mechanism follows from these kinetic results in sulphuric acid, and in nitric acid, though they are consistent with what is deduced; but the zeroth-order kinetics in organic solvents, and its transition to first-order kinetics with diminishing aromatic reactivity, proves without alternative the formation and effectiveness of the nitronium ion, NO_2^+. The kinetically fundamental process is shown to be localised in nitric acid, to be activated, to be heterolytic, and to produce electron-deficient nitrogen. Therefore it is the bond-fission

$$HO\text{—}\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}O_2 \longrightarrow HO^- + NO_2^+$$

disregarding the associated, instantaneous proton-transfers, which are treated under (2).

(2) *Solute Effects on Nitration Kinetics: Mechanism of Formation of the Nitronium Ion* (p. 2412).—Aromatic nitration in nitric acid, or in nitromethane, or acetic acid, with nitric acid in constant excess, is accelerated by sulphuric acid, and retarded by ionising nitrates, the latter effect being specific, and not a general salt effect. The effect of sulphuric acid on the rate, and that of nitrate ion on the reciprocal of the rate, obey linear limiting laws. The effects occur alike with zeroth- and first-order reactions, always without disturbance to the reaction order. These results show that one proton is employed, and one nitrate ion eliminated, in the conversion of nitric acid into a nitronium ion; and that these changes are reversed. It also follows that they take place in an earlier reaction-step than that which produces nitronium ion, because a zeroth-order nitration only maintains its kinetic order when the latter step is not reversed. Thus the following two-stage mechanism is unequivocally established:

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \text{ (fast)}$$

$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O \text{ (slow)}$$

Consistently, the kinetic effect of water in zeroth-order nitration is negligible in comparison with that of nitrate ion. Relatively large amounts of water will retard the nitration by reversing the second of the above reaction-steps; but then the zeroth-order reaction goes over into a first-order reaction. Consistently also, the kinetic effect of water on first-order nitration is comparable to that of nitrate ion. These considerations establish the formation of the nitric acidium ion, $H_2NO_3^+$. The function of one of the above-written nitric acid molecules is simply to supply a proton to the other one, which is the actual source of the nitronium ion; and the function of proton-supply will obviously be taken over by a stronger acid than nitric acid, such as sulphuric acid, if such an acid is present.

(3) *Medium Effects on Nitration Kinetics: Mode of Action of the Nitronium Ion* (p. 2423).—Acetic acid, nitromethane, nitric acid, and sulphuric acid, considered as nitration media, form a series in order of increasing polarity. A partial or complete replacement of acetic acid by nitromethane, of either by nitric acid, or of any of these by sulphuric acid, increases nitration rate, independently of reaction order. Such changes to more polar media may also change the order, reducing it from first towards zeroth, as has been illustrated for the replacement of acetic acid by nitromethane, and for its partial replacement by nitric acid. From these results, and the well-established theory of kinetic solvent effects, it follows that, while ionic charges are created in the reactions that produce the nitronium ion, ionic charges are neither formed nor destroyed in the kinetically significant step of the attack by the nitronium ion on the aromatic molecule. The nitrating attack must therefore be a two-stage bimolecular process:

$$ArH + NO_2^+ \longrightarrow \overset{+}{A}rH(NO_2) \text{ (slow)}$$

$$\overset{+}{A}rH(NO_2) \longrightarrow ArNO_2 + H^+ \text{ (fast)}$$

The slowness of the first step is shown by the kinetics, and the relative rapidity of the second is confirmed (Melander) by the absence of a hydrogen-isotope effect on the rate. The recently discussed suggestion that the nitrating attack is a one-stage termolecular process, requiring the collaboration of a base, and especially of an anion, as in the equation

$$NO_2^+ + ArH + HSO_4^- \longrightarrow ArNO_2 + H_2SO_4$$

is thus disproved: for this reaction, which destroys charges, should be strongly retarded by polar solvents; and it should show a hydrogen-isotope effect. The very limited kinetic effects which formed the basis of this theory can reasonably be ascribed in part to the secondary influence of charge distribution, and in part to the formation of salt-like complexes by the aromatic compounds under the conditions of the observations (Gillespie, Millen).

(4) *Effects of Nitrous Acid on Nitration Kinetics: Condition of Nitrous Acid in Nitric Acid Solvents* (p. 2430).—The term "nitrous acid" is used to cover all materials in nitric acid which after dilution with water could be together estimated as nitrous acid. Aromatic nitration in nitric acid, or in nitromethane, or acetic acid, with nitric acid in constant excess, is retarded by "nitrous acid," which itself is neither formed nor destroyed, except in some special cases considered elsewhere (Part VI *et seq.*). The effect applies alike to zeroth-order and first-order reactions, and operates always without disturbance to the reaction order. At low nitrous acid concentrations, and in the absence of water, the effect on the reciprocal of the rate is linear with respect to the power one-half of the nitrous acid concentration. At higher nitrous acid concentrations, or in the presence of water, a stronger retarding effect appears. With sufficient nitrous acid and water, the reciprocal of the rate varies with the three-halves power of the nitrous acid concentration. These effects are attributed to the ionisation of oxides of nitrogen by nitric acid. Nitrous acid exists in nitric acid mostly as dinitrogen tetroxide; but an increase of concentration, or the addition of water, increases the small proportion in which it exists as dinitrogen trioxide:

$$2N_2O_4 + H_2O \rightleftharpoons N_2O_3 + 2HNO_3$$

Dinitrogen tetroxide and dinitrogen trioxide are ionised thus:

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

The nitrate ion deprotonates the nitric acidium ion, as has been described under (2). The nitrite ion acts similarly, but, as the stronger base, its effect is specifically more powerful. Deprotonation by the nitrate ion leads to retardation by the one-half-power law, and deprotonation by the nitrite ion to retardation by the three-halves-power law.

(0) Introduction to Some Papers of Several Concurrent Series.

(0.1) *This Paper as a Development of Previous Work on Nitration Kinetics.*—The work now reported is a continuation of the investigation, described in Part I * (Benford and Ingold, *J.*, 1938, 929), into the kinetics of nitration of aromatic compounds by nitric acid in homogeneous solution. We have employed the dilatometric technique used by Benford and Ingold (*loc. cit.*), adding some small refinements which will be mentioned later. As heretofore, the interpretation of the dilatometric results has been controlled by chemical analysis. A short statement of our main results and conclusions has already been published (Hughes, Ingold, and Reed, *Nature*, 1946, **158**, 448).

Having established a convenient technique, Benford and Ingold made a general survey of solvents for nitration. These they classified as fast, medium, and slow, according to their effect on nitration rate. Thus sulphuric acid was a fast solvent, nitromethane a medium-rate solvent, and acetic acid was a slow solvent. In consequence of earlier work by Martinsen and others, much was already known about the kinetics of nitration in sulphuric acid; and therefore, Benford and Ingold concentrated upon the medium-rate solvent, nitromethane, leaving for the future the study of slow, and the continued study of fast, solvents.

A further investigation was promised in Part I on the kinetics of nitration in sulphuric acid, and a programme of work on these lines was commenced; but it was abandoned when, later, the information was received that others were engaged in a similar study. However, we continued our investigation of nitration kinetics and mechanism in a large number of other ways, of which the following three are brought together in the present paper.

First, in order to strengthen the evidence concerning fast solvents, we have studied nitration kinetics with nitric acid itself as the solvent: though not so fast as sulphuric acid, nitric acid is certainly to be classed as a fast solvent for nitration.† Secondly, we have extended, and in a sense completed, the kinetic investigation of Benford and Ingold on nitration in the medium-rate solvent, nitromethane. Thirdly, as foreshadowed in Part I, we have carried out a similarly full investigation on the kinetics of nitration in the slow solvent, acetic acid. Judged from the results, the solvents mentioned might fairly be classified into two main groups: sulphuric acid and nitric acid are more or less comparable, and so also are nitromethane and acetic acid, the differences in each case being quantitative rather than qualitative.

* The paper to which we refer as Part I of the present series was published under the specific title "A Dilatometric Investigation of the Kinetics of Aromatic Nitration, especially in Nitromethane Solution."

† Perchloric acid is stated to be a faster solvent for nitration than is sulphuric acid (Robinson, *J.*, 1941, 238), though no detailed report illustrating the comparison is yet available.

(0.2) *Continued Study of Nitration Kinetics in the Accompanying Papers.*—We have extended the kinetic investigation in several further directions. First, the very slow nitration solvent, water, required to be examined, in order to complete the representation of solvent types. The issues here involved are rather distinct, and it thus became convenient to describe this part of the work in a separate paper (Part III). Secondly, all the work so far mentioned is concerned with nitrations effected by the use of nitric acid, either alone or in a solvent; but alkyl and acyl nitrates are also in principle nitrating agents, and thus it seemed desirable to investigate their behaviour. A particularly important special case is that of nitryl nitrate, *i.e.*, dinitrogen pentoxide. Some further papers of the present group deal with this part of the subject (Parts IV and V).

Thirdly, the general kinetic findings, as set out in the present paper, apply without modification to a great variety of aromatic substances; but derivatives of phenol and aniline form a special class, inasmuch as their nitration often involves complications, which affect the kinetics, and sometimes also the products, of nitration. The nature of these disturbances, and their place in the general scheme of aromatic nitration, is examined in other papers of the present collection (Parts VI—VIII). However, our work on the kinetics of nitration of aniline derivatives is still incomplete, and further papers on this section of the subject will be offered later.

(0.3) *Non-kinetic Study of Nitrating Agents as Reported in Accompanying Papers.*—This explanation of the plan of the present work has referred as yet only to kinetic investigations. In the study of reaction mechanism, it is desirable, where possible, to combine kinetic with non-kinetic evidence; and, accordingly, the papers mentioned above will be found interspersed with a number of others, which largely follow their own general theses, but in doing so contribute evidence of a non-kinetic kind on the mechanism of nitration.

Such evidence has been obtained in several different ways, including the physical examination of nitrating media, the chemical separation of reactive entities contained in such media, and the physical study of the isolated entities. We may refer to accompanying papers, or series of papers, under the serial titles, "Cryoscopic Measurements in Sulphuric Acid," Cryoscopic Measurements in Nitric Acid," "Chemistry of Nitronium Salts," "Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen," and "Chemistry of Nitroammonium Salts." The physical properties which have been found to be of most service in this problem are freezing-point depressions, Raman spectra, and electrolytic phenomena; and the relevant work by the first two of these methods is being published at this time. Our electrochemical work, however, it still unfinished, as is also some work which employs the method of infra-red absorption spectra. Papers dealing with these divisions of the investigation will be published later. A related crystallographic investigation is proceeding in Professor Cox's laboratory.

(1) Kinetic Orders of Aromatic Nitration: The Nitronium Ion, NO_2^+.

(1.0) *Conditions affecting Reaction Order.*—The kinetic results which are the simplest to interpret, and are of the most general significance with respect to the mechanism of nitration, are those which relate to kinetic order, and its variation with the aromatic compound and with the solvent.

Summarising our previous remarks on the general differences between solvents, we now arrange them, as shown below, in a graded series, according to their effect on reaction rate. The reason for doing this is that the same series forms a useful basis for considering the behaviour of the different solvents in the determination of the kinetic order of nitration, and for discussing the effects of the solvents on reaction mechanism:

$$H_2SO_4 > HNO_3 \gg CH_3{\cdot}NO_2 > CH_3{\cdot}CO_2H \gg H_2O$$

For the purpose of discussing the effect of the constitution of the aromatic compound on reaction order and mechanism, it is convenient to grade also aromatic compounds with reference to their influence on nitration rate, *i.e.*, according to the relative rates at which they would be attacked under uniform conditions.

This can be discovered by what we may call the competition method: two aromatic compounds, both in excess, are allowed to compete for a limited amount of a nitrating agent in the same homogeneous solution, and, from the proportions in which they are nitrated, the ratio of the specific rates at which the nitrating entity attacks the competing aromatic molecules is calculated.

Determinations on these lines have been made for benzene and a number of monosubstituted benzenes (Ingold and Shaw, *J.*, 1927, 2918; Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959; Ingold and Smith, *J.*, 1938, 905; Bird and Ingold, *J.*, 1938, 918; Bordwell and Rohde, *J. Amer. Chem. Soc.*, 1948, **70**, 1191; Ingold and Shaw, *J.*, 1949, 575). The numerical results vary with the conditions, but are not very sensitive to them; so that the following statements may be taken as approximately true over a considerable range of temperatures and nitrating media. Toluene is attacked 24 times faster than benzene, fluoro- and iodo-benzene 6 times more slowly than benzene, chloro- and bromo-benzene 30 times more slowly than benzene, and ethyl benzoate 300 times more slowly than benzene. Qualitatively we know that benzenesulphonic acid is attacked still more slowly, and nitrobenzene even more slowly. Thus the relative effects of substituents in activating or deactivating the benzene nucleus towards this type of attack is expressed by the following sequence:

$$\mathrm{Me} > (\mathrm{H}) > \mathrm{F},\ \mathrm{I} > \mathrm{Cl},\ \mathrm{Br} > \mathrm{CO_2Et} > \mathrm{SO_3H} > \mathrm{NO_2}$$

There is reason to believe that, within fairly wide limits, these relationships will hold qualitatively for polysubstituted benzenes; so that, for instance, *p*-xylene is attacked more rapidly than toluene, and *p*-dichlorobenzene more slowly than chlorobenzene. We shall later confirm this expectation by means of rate-constants applying to such examples.

(1.1) *Observations on Kinetic Order.*

(1.1.1) *Reaction Order in Sulphuric Acid.*—Before the inception of this work, a simple kinetic order for the nitration of aromatic compounds had been established for one solvent only, *viz.*, sulphuric acid. The nitration of benzene itself by nitric acid in sulphuric acid is too rapid for measurement; but in 1904 Martinsen found that the nitration of nitrobenzene in this medium was a straightforward reaction of the second order (*Z. physikal. Chem.*, 1904, **50**, 385); and he later obtained the same result for several other benzene derivatives, such as 2 : 4-dinitrotoluene and the three nitrobenzoic acids (*ibid.*, 1907, **59**, 605). This result has been confirmed by all subsequent investigators. Klemenc and Schöller observed second-order kinetics for the nitration, in sulphuric acid, of several more benzene derivatives, such as 2 : 4-dinitro-*m*-xylene and the chloronitrobenzenes (*Z. anorg. Chem.*, 1924, **141**, 231). Lauer and Oda established corresponding kinetics for the nitration of anthraquinone (*J. pr. Chem.*, 1936, **144**, 176; *Ber.*, 1936, **69**, 1061); as did Oda and Ueda for the nitration of a number of substituted anthraquinones (*Bull. Inst. Phys. Chem. Res., Japan*, 1941, **20**, 335). Westheimer and Kharasch, besides confirming a number of the earlier results, have established second-order kinetics for the nitration in sulphuric acid of some additional nitro-substituted benzenes, and also of some derivatives of benzoic acid and benzenesulphonic acid (*J. Amer. Chem. Soc.*, 1946, **68**, 1871). Bennett, Brand, James, Saunders, and Williams have supplied further confirmation of Martinsen's observation that the nitration of 2 : 4-dinitrotoluene in sulphuric acid is a second-order process (*J.*, 1947, 474).

The general conclusion from all this work may be epitomised thus:

$$\left.\begin{array}{c}\text{Rate in } \mathrm{H_2SO_4} = k_2[\mathrm{HAr}][\mathrm{HNO_3}] \\ \text{[Shown for nitro-substituted benzenes, for benzoic and benzenesulphonic acids, and for anthraquinones (lit.).]}\end{array}\right\} \quad . \quad . \quad (1)$$

(1.1.2) *Reaction Order in Nitric Acid.*—With the above conclusion we can associate one, which is derived in the present paper, concerning nitrations in which nitric acid is, not only the nitrating agent, but also the solvent. In these experiments the nitric acid was, of course, in constant concentration. The reactions were found to be of the first order with respect to the aromatic compound, and hence the kinetic equation for nitration in nitric acid is consistent with that given above for nitration by nitric acid in sulphuric acid.

The aromatic compounds studied were nitrobenzene, *p*-chloronitrobenzene, and 1-nitroanthraquinone. The course of a typical run is shown in Fig. 1. From the linear fall with time shown by the logarithm of the concentration of the compound undergoing nitration, it is evident that the first-order rate-law is well obeyed.

Some first-order rate constants for nitration in nitric acid are reported in Table I: other values will be found in Tables VII, XII, XIV, and XXIII, on pp. 2414, 2417, 2418, and 2433 respectively.

TABLE I.

First-order rate constants (k_1 *in sec.*$^{-1}$) *for nitration in nitric acid.*

Expt.		$[HNO_3]$.	Temp.	$[HAr]_0$.	10^5k_1.
410	Nitrobenzene	0·0015	−13·3°	0·20	547
560	*p*-Chloronitrobenzene	0·03	+20·0°	0·15	1·37
571	1-Nitroanthraquinone	0·0035	+20·0°	0·24	248

Nitrating solutions nearly always contain what for convenience we call " nitrous acid " and symbolise HNO_2, that is, lower oxides of nitrogen and all other materials which in the water-diluted solution are collectively estimated as nitrous acid. In most conditions this nitrous acid has a definite (usually a negative) catalytic effect, and therefore it is necessary to include its concentration among the particulars which must be specified when quoting rate constants.

FIG. 1.

Nitration in nitric acid: general kinetic form (illustrated by Expt. 411 *on the nitration of nitrobenzene at* −13·3°).

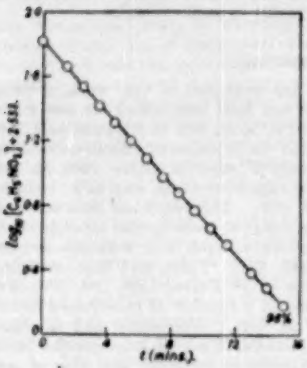
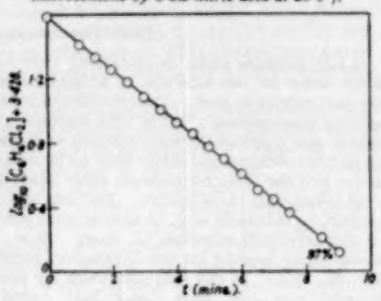


FIG. 2.

Nitration in nitromethane. First-order kinetic form (illustrated by Expt. 301 *on the nitration of* p*-dichlorobenzene by* 8·5*M-nitric acid at* 20·0°).



This is done in Table I, and in all the later tables of this paper. But in the experiments of Table I the concentrations of nitrous acid were too small to have significant effects on the rate constants, excepting possibly in the experiment on *p*-chloronitrobenzene.

In the example of 1-nitroanthraquinone we investigated the effect of adding sulphuric acid to the medium, thus tracing part of the transition from a nitric acid to a sulphuric acid solvent. This increased the reaction rate, as we shall note in more detail later; but, the nitric acid being always in constant excess, it made no difference to the reaction order. Moderate additions of water, of certain salts, including nitrates, and of nitrous acid also made no difference to the reaction order.

Thus our general result for nitric acid solvents may be summarised as follows:

$$\left.\begin{array}{c}\text{Rate in } HNO_3 = k_1[HAr] \qquad ([HNO_3] = \text{constant}) \\ \text{[Shown for nitrobenzene, } p\text{-chloronitrobenzene and 1-nitroanthraquinone (this paper).]}\end{array}\right\} \quad \ldots \quad (2)$$

(1.1.3) *Reaction Orders in Nitromethane.*—The first well-defined kinetic results in any solvent other than sulphuric acid were those reported in Part I (Benford and Ingold, *loc. cit.*). With nitromethane as solvent and nitric acid in constant excess, zeroth-order kinetics were demonstrated for the nitration of benzene and two of its homologues. This means that nitration proceeds at an undiminished rate until the original substance is exhausted, when the reaction has to cease abruptly. Such insensitiveness of the rate to the concentration of the aromatic compound seems to imply an insensitiveness to the nature of the compound, and within limits

this was confirmed: in the same medium and at the same temperature, benzene, toluene, and ethylbenzene were all nitrated at an identical rate:

$$\left.\begin{array}{l}\text{Rate in Me·NO}_2 = k_3 \qquad ([HNO_3] = \text{constant})\\ \text{[Shown for benzene, toluene, and ethylbenzene (Part I).]}\end{array}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

These relationships appear to be restricted to benzene and those derivatives of benzene, which, if tested by the competition method, would be found to be attacked by nitrating agents more rapidly than benzene. The relationships do not hold for those aromatic compounds which, by the competitive test, would be found to be substantially less reactive than benzene. This was illustrated in Part I with reference to the four halogenobenzenes. These compounds divide themselves into two pairs, just as they do in the rate series based on the competition test. In nitromethane solution with nitric acid in constant excess, fluoro- and iodo-benzene are nitrated at nearly identical rates, which are rather smaller than the common rate applying to benzene, toluene, and ethylbenzene; and the rates for fluoro- and iodo-benzene are not quite constant, but depend slightly on the concentration of the halogeno-compound, the degree of dependence increasing towards the end of reaction. For chloro- and bromo-benzene the rates are again nearly identical, but are notably smaller than for the other two halogeno-compounds; and they now have a greater degree of dependence on the concentration of the halogeno-compound, this dependence increasing nearly to proportionality towards the end of reaction.

Benford and Ingold interpreted these results as indicating kinetics having intermediate character between two simple limiting forms. One limiting form was obviously to be identified with the zeroth-order kinetics which had been established for benzene and two of its homologues. Corresponding to their distribution in the rate series, fluoro- and iodo-benzene took positions fairly close to this limit, while chloro- and bromo-benzene occupied more remote places, nearer the other limit. This second limiting form was hypothetically identified with a first-order type of kinetics, which was assumed to be observable for nitration in nitromethane with still less reactive aromatic compounds, but which Benford and Ingold did not in fact observe directly:

$$\left.\begin{array}{l}\text{Rate in Me·NO}_2\text{: intermediate between (3) and (5)}\\ \text{[Shown for the four halogenobenzenes (Part I).]}\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We have confirmed this identification of the second limiting kinetic form by isolating it—how completely can be seen from the example represented in Fig. 2. To achieve this result, all that was necessary was to reduce further the reactivity of the aromatic ring, as it would appear in experiments on competitive nitration, by the introduction of a second halogen atom. The linear time-dependence of the logarithm of the concentration of the substance undergoing nitration shows the reaction to be of the first order.

Some first-order rate constants for *p*-dichlorobenzene and 1 : 2 : 4-trichlorobenzene are given in Table II. Other values for the former substance will be found in Tables XI and XXI on pp. 2416 and 2431, respectively. These reactions are sensitive to anti-catalysis by nitrous acid, even at the lowest concentrations here recorded. However, the kinetic order remains unaffected by changes in the concentration of the nitrous acid, or of the nitric acid, within the range of our experiments.

TABLE II.

First-order rate constants (k_1 *in sec.*$^{-1}$) *for nitration in nitromethane.*

Expt.	HAr.	$[HNO_3]_0$.	$[HNO_3]_t$.	Temp.	$[HAr]_0$.	10^4k_1.
165	*p*-Dichlorobenzene	8·5	0·0135	10·0°	0·20	165
166	,,	,,	,,	19·9	,,	371
150	,,	,,	0·0240	20·0	0·10	367
301	,,	,,	0·0018	,,	,,	649
300	,,	,,	,,	,,	0·17	617
299	1 : 2 : 4-Trichlorobenzene	,,	,,	,,	0·10	54·4
156	*p*-Dichlorobenzene	11·5	0·0269	,,	,,	2470

The fact that the first-order kinetic form of nitration, which, on deactivating the aromatic ring by successive chlorine substituents, is reached at *p*-dichlorobenzene, is not still transitional, but is a stable limiting kinetic form, is proved by introducing the third chlorine atom of 1 : 2 : 4-trichlorobenzene. This makes no difference to the first-order form of the reaction, although, as the rate-constants themselves establish, it does bring about a further reduction in the reactivity of the aromatic ring towards the nitrating agent.

Summarising this series of results in the form already used for other series, we have

$$\left.\begin{array}{l}\text{Rate in Me-NO}_2 = k_1[\text{HAr}] \qquad ([\text{HNO}_3] = \text{constant})\\ [\text{Shown for } p\text{-di- and } 1:2:4\text{-tri-chlorobenzene (this paper).}]\end{array}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

(1.1.4) *Reaction Orders in Acetic Acid.*—Benford and Ingold thought that the kinetic forms that they had established for nitration in nitromethane, and, in particular, the zeroth-order kinetics followed by the nitration of benzene and its homologues, were dependent in a special way upon that solvent; but we have now observed all the same kinetic phenomena with acetic acid as the solvent. As compared with nitromethane, the use of acetic acid as solvent produces, not only reduced rates, but also a distinct shift in the distribution of the aromatic compounds among the different reaction orders. Thus, under the conditions we have used, the nitration of benzene itself in acetic acid is not invariably a reaction of zeroth order, as it is in nitromethane. With certain concentrations of nitric acid the reaction is nearly of zeroth order; but at other concentrations the deviations from zeroth-order kinetics are very appreciable; and at yet others they are large. However, the nitration of toluene is definitely of zeroth order over the whole of the investigated range of concentrations, and the same is true for all the higher homologues of benzene that we have examined, *viz.*, ethylbenzene, *p*-xylene, and mesitylene. Fig. 3 illustrates the general form of the kinetic results obtained for the nitration of the alkylated benzenes in acetic acid. The same form of curve is obtained for benzene itself provided that the concentration of nitric acid is above a certain minimum.

Some zeroth-order rate constants applying to nitrations in acetic acid are given in Table III. In Expts. 79 and 80, the concentration of nitric acid was made large in order to secure a zeroth-order reaction for benzene; and then, because of the high resulting rates, the concentration of

TABLE III.

Zeroth-order rate constants (k_0 *in sec.*$^{-1}$ *g.-mol.l.*$^{-1}$) *for nitration in 99·8% acetic acid.*

Expt.	HAr.	$[HNO_3]_0$.	$[HNO_3]_t$.	Temp.	$[HAr]_0$.	10^4k_0.
79	Benzene	12·4	0·497	10·7°	0·35	97
80	Toluene	,,	,,	,,	0·33	103
54	,,	7·0	0·0024	20·0	0·20	6·28
55	,,	,,	0·0044	,,	0·10	6·43
60	,,	,,	0·0050	,,	0·10	5·90
53	,,	,,	0·0060	,,	0·05	6·50
56	Ethylbenzene	,,	0·0027	,,	0·04	6·00
61	,,	,,	0·0046	,,	0·10	6·20
57	,,	,,	0·0143	,,	0·10	5·65
62	*p*-Xylene	,,	0·0046	,,	0·10	6·17
51	,,	,,	0·0192	,,	0·07	5·70
50	Mesitylene	,,	0·0037	,,	0·05	5·63
63	,,	,,	0·0046	,,	0·10	5·62
52	,,	,,	0·0073	,,	0·09	5·48
48	*p*-Xylene	5·0	0·0096	,,	0·06	0·433
49	Mesitylene	,,	0·0137	,,	0·07	0·417

nitrous acid was also made unusually large in order to bring the rates down to values which could be measured conveniently. In all the other experiments of Table III the kinetic effect of nitrous acid is small if not negligible.

The most severe test for a zeroth-order reaction is that the rate shall be independent, not only of the concentration of the substance nitrated, but also of the nature of that substance, provided that the nitration medium and temperature remain the same. Table III shows that this criterion is satisfied within the range of our experiments.

We may summarise these findings in the following statement:

$$\left.\begin{array}{l}\text{Rate in HOAc} = k_0 \qquad ([\text{HNO}_3] = \text{constant})\\ [\text{Shown conditionally for benzene, and generally for toluene, ethylbenzene,}\\ p\text{-xylene, and mesitylene (this paper).}]\end{array}\right\} \quad . \quad . \quad (6)$$

When the kinetics of the nitration of benzene in acetic acid containing nitric acid in constant excess differ appreciably from those of a zeroth-order reaction, the deviation is always in the direction of one which would be caused by an admixed first-order reaction; and the first-order character becomes more marked towards the end of reaction. Fig. 4 illustrates the course of a nitration of benzene in acetic acid with such a concentration of nitric acid that the deviation

from zeroth-order kinetics is large. In order to show the character of the deviation, both the concentration of the benzene and the logarithm of its concentration have been plotted against time. Though the reaction has no definite kinetic order, a resemblance to first-order kinetics can be recognised: a quoted first-order rate constant, based on the latter part of the reaction, would have some rough significance.

FIG. 3.

Nitration in acetic acid. Zeroth-order kinetic form (illustrated by Expt. 57 on the nitration of ethylbenzene by 7M-nitric acid at 20·0°).

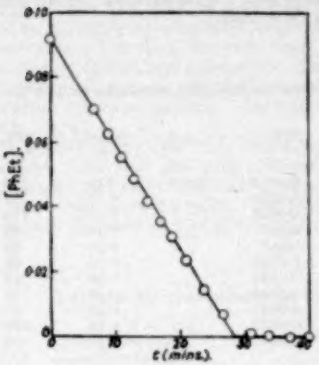


FIG. 4.

Nitration in acetic acid. Mixed-order kinetics (illustrated by Expt. 110 on the nitration of benzene by 9·7M-nitric acid at 20·0°).

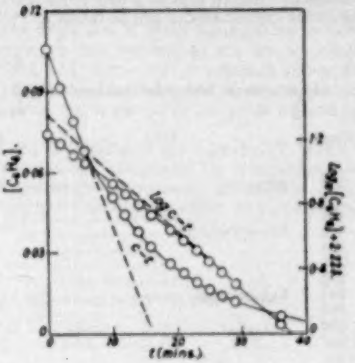


FIG. 5.

Nitration in acetic acid. Nearly complete transition to first-order kinetics (illustrated by Expt. 176 on the nitration of chlorobenzene by 10·0M-nitric acid at 20·0°).

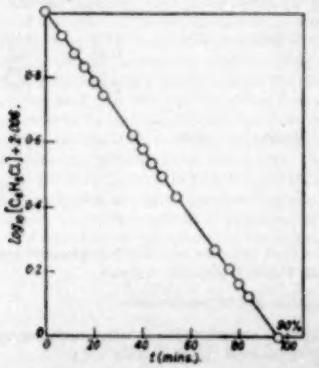
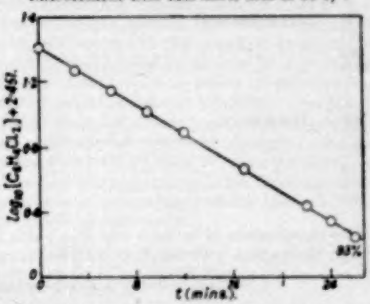


FIG. 6.

Nitration in acetic acid. First-order kinetic form (illustrated by Expt. 164 on the nitration of p-dichlorobenzene with 12M-nitric acid at 19·9°).



Kinetically, the nitration of benzene in acetic acid is somewhat similar to that of fluoro- or of iodo-benzene in nitromethane. The nitration of these two halogenobenzenes in acetic acid, containing a constant excess of nitric acid, follows a kinetic form which is intermediate between zeroth and first order, but under most conditions, and especially towards the end of reaction, is close enough to the latter to give approximate significance to a quoted first-order

rate constant. Thus the nitrations of fluoro- and iodo-benzene in acetic acid are kinetically rather similar to the nitrations of chloro- and bromo-benzene in nitromethane. The nitrations of the last two halogenobenzenes in acetic acid, containing a constant excess of nitric acid, follow first-order kinetic forms in fairly close approximation, as is illustrated for chlorobenzene by the linearity of the logarithmic plot in Fig. 5. The fact that the reaction order is still not quite integral can, however, be shown by comparisons among first-order rate constants derived from experiments, similar to that illustrated, but with different initial concentrations of the halogenobenzene.

Table IV contains a number of approximate first-order rate constants computed for such mixed-order nitrations of benzene and the halogenobenzenes in acetic acid as have kinetic forms sufficiently close to that of a first-order reaction to allow such a representation. Other similar values for chlorobenzene will be found in Table XXII on p. 2432.

TABLE IV.

Approximate first-order rate-constants (k_1 *in sec.*$^{-1}$) *for mixed-order nitrations in 99·8% acetic acid.*

Expt.	HAr.	$[HNO_3]_0$.	$[HNO_2]_0$.	Temp.	$[HAr]_0$.	10^3k_1.
	Series A:					
120	Benzene	8·0	0·0015	20·0°	0·10	118
257	,,	,,	0·0035	,,	0·10	126
124	,,	,,	0·0042	,,	0·10	113
262	Fluorobenzene	,,	small	,,	0·10	30
264	,,	,,	small	,,	0·10	30
259	,,	,,	0·0041	,,	0·10	26
252	,,	,,	0·0043	,,	0·16	25
267	Iodobenzene	,,	0·0039	,,	0·10	30
266	,,	,,	0·0043	,,	0·10	27
258	,,	,,	0·0057	,,	0·16	27
256	,,	,,	0·0072	,,	0·10	29
	Series B:					
277	Fluorobenzene	9·0	0·0043	20·0	0·10	114
278	,,	,,	,,	,,	0·20	100
275	Iodobenzene	,,	,,	,,	0·10	137
274	Chlorobenzene	,,	,,	,,	0·10	52
271	Bromobenzene	,,	,,	,,	0·10	45
279	,,	,,	,,	,,	0·20	39
	Series C:					
293	Chlorobenzene	10·0	0·0022	20·0	0·05	365
291	,,	,,	,,	,,	0·10	325
292	,,	,,	,,	,,	0·23	294
294	,,	,,	,,	,,	0·30	281
	Series D:					
108	Benzene	9·7	0·457	20·0	0·10	167
107	,,	,,	,,	,,	0·17	137
105	,,	,,	,,	,,	0·17	133
110	,,	,,	,,	,,	0·21	124
109	,,	,,	,,	,,	0·30	85
113	,,	,,	,,	,,	0·34	75

The experiments of Series A and B in Table IV show that benzene and the halogenobenzenes arrange themselves with reference to nitration rate into three groups, as follows:

benzene > fluoro- and iodo-benzene > chloro- and bromo-benzene

The grouping is the same as in Benford and Ingold's kinetic experiments in nitromethane, and the same as in Bird and Ingold's comparisons by the competition method (*locc. cit.*).

The data of Series C in Table IV show that the nitration of chlorobenzene in 10M-nitric acid is not accurately a reaction of the first order. No doubt it would be very nearly of first order in sufficiently dilute solution; but as the initial, and therefore the average, concentration of the aromatic compound is increased in successive experiments, the average reaction-order falls, and therefore the computed average first-order rate constant falls. This is consistent with the observation that, in any one experiment, the instantaneous reaction-order rises as the

concentration of the chlorobenzene falls towards the end of the experiment. The figures of Series D show the same thing for the nitration of benzene in 9·7M-nitric acid. As Fig. 4 illustrates, this reaction is certainly not accurately obeying a first-rate law.

We may express these findings in a summarising statement, as follows:

Rate in HOAc: Intermediate between (6) and (8)
[Shown for benzene and the four halogenobenzenes (this paper).] . . . (7)

As was explained above, one of the two limits which bound this range of intermediate kinetic forms, *viz.*, the zeroth-order form, has been established as a stable limit for nitration in acetic acid by the study of benzene homologues containing from one to three activating alkyl groups. The other limit, *viz.*, the first-order form of reaction, has been similarly established as a stable limit by the study of benzene derivatives containing from one to three deactivating chlorine substituents. The same first-order form is preserved in the presence of the more strongly deactivating carbethoxyl substituent. In acetic acid, with nitric acid in constant excess, the nitrations of *o*-, *m*-, and *p*-dichlorobenzene, of 1 : 2 : 4-trichlorobenzene, and of ethyl benzoate, all display first-order kinetics. The course of a typical run is shown as the usual logarithmic plot in Fig. 6.

A number of first-order rate constants for nitration in acetic acid are assembled in Table V. The rates show that the three chlorine atoms successively introduced in the chlorinated benzenes studied exert deactivating effects, which, although not equal to one another, are of the same order of magnitude. They show also that the deactivating effect of a carbethoxyl group is of the order of that of two chlorine atoms.

TABLE V.

First-order rate constants (k_1 *in sec.*$^{-1}$) *for nitrations in* 99·8% *acetic acid.*

Expt.	HAr.	$[HNO_3]_0$.	$[HNO_2]_0$.	Temp.	$[HAr]_0$.	10^4k_1.
282	*o*-Dichlorobenzene	10·5	0·0029	20·0°	0·10	25·7
283	*m*-Dichlorobenzene	"	"	"	"	49·8
281	*p*-Dichlorobenzene	"	"	"	"	20·0
280	Ethyl benzoate	"	"	"	"	15·5
161	*p*-Dichlorobenzene	12·0	0·0030	10·0	0·10	67·6
164	"	"	"	19·9	"	165
310	"	12·2	0·0034	20·0	0·10	223
311	1 : 2 : 4-Trichlorobenzene	"	"	"	"	18·0

The differences between the rates for the isomeric dichlorobenzenes, in particular the greater rate of nitration of *m*-dichlorobenzene than of its isomers, may possibly be correlated with the circumstance that both the chlorine atoms of *m*-dichlorobenzene are, like the single chlorine atom of chlorobenzene, in *ortho*- or *para*-positions with respect to the principal positions into which the nitro-group enters; whereas only one of the two chlorine atoms in *o*- or in *p*-dichlorobenzene, and only two of the three in 1 : 2 : 4-trichlorobenzene are in *ortho*- or *para*-positions with respect to the main positions in which nitration occurs in these substances. One chlorine atom in each of these three compounds necessarily occupies a *meta*-position with respect to the principal positions of nitration. From the orientational effects of halogens, one must expect deactivation by chlorine to be stronger in the *meta*-position than in other positions. On the other hand, the figures themselves show that the deactivating actions of the different chlorine atoms in the polysubstituted compounds are by no means independent of one another.

We summarise this group of the results in the following statement:

Rate in HOAc = k_1[HAr] ($[HNO_3]$ = constant)
[Shown for *o*-, *m*- and *p*-dichlorobenzene, 1 : 2 : 4-trichlorobenzene, and ethyl benzoate (this paper).] . . . (8)

(1.2) *Discussion (Part I). The Kinetic Orders: Formation and Effectiveness of the Nitronium Ion.*

(1.2.1) *Significance of the Changes of Kinetic Order: The Nitronium Ion.*—The following facts requires explanation. Nitration is rapid, and exhibits second-order kinetics in sulphuric acid (equation 1): it is rather rapid, and exhibits first-order kinetics in nitric acid (equation 2). In the organic solvents, nitromethane and acetic acid, with nitric acid in constant excess, nitration is relatively slow; and it exhibits zeroth-order kinetics if the aromatic compound is

sufficiently reactive in electrophilic substitutions (equations 3 and 6), first-order kinetics if the aromatic compound is sufficiently unreactive in such substitutions (equations 5 and 8), and mixed zeroth-to-first-order kinetics for aromatic compounds having intermediate reactivity (equations 4 and 7).

The second-order nitration in sulphuric acid and the first-order nitration in nitric acid could be held to be consistent with many theories of mechanism. These kinetics indicate nitration either by the nitric acid molecule itself, or by any reactive entity whose concentration throughout nitration bears a constant ratio to the stoicheiometric concentration of nitric acid. In the latter alternative, the nitrating entity might be formed nearly completely, partially, or in minute proportion; but it must be formed rapidly in comparison with the rate of its involvement in nitration. That is all that can be said on the basis of these particular kinetic results: they are of too normal a type to give any specific indication of mechanism.

On the other hand, the observation of zeroth-order kinetics for nitration in nitromethane and in acetic acid is highly significant. It has for nitration the same kind of importance as Lapworth's discovery of the first-order bromination of acetone had for prototropy, a general reaction which we now know to be rate-controlled by a protolysis. Again, the observation that, for nitration in these solvents, the kinetic order changes during a graded series of constitutional changes related to the reactivity of the aromatic molecule for electrophilic substitution, has the same significance for nitration as the discovery of a similar change of kinetic order, during a progressive change of alkyl structure in nucleophilic aliphatic substitution, had for the mechanism of that general reaction. In the latter case, the accepted interpretation is that the alkyl derivative undergoes a heterolysis which, if sufficiently facilitated by internal polar effects, becomes rate-determining for the substitution, independently of co-operation by the second reactant.

Apart from the lead given by these known analogies, the conclusion indicated by the changes of kinetic order is clear. Nitration depends on some preliminary process which does not involve the aromatic compound, and which, by the use of solvents such as nitromethane and acetic acid, can be made slow enough to be rate-determining, provided that a sufficiently reactive aromatic compound is employed. The preliminary change cannot be in the solvent, because solvents which have little in common with respect to their general chemistry behave similarly. Hence it must be in the nitric acid itself. Benford and Ingold's original assumption that, for nitration in nitromethane, the preliminary change consisted in the prototropic isomerisation of the solvent is easily shown to be incorrect. For if it were true, the rate of a zeroth-order nitration in nitromethane should be equal to the rate at which nitromethane would be brominated in identical conditions, apart from the replacement of the aromatic compound by bromine. Actually the former reaction is enormously faster than the latter. Further, the rates of the two processes are changed in opposite ways by changes in the concentration of nitric acid.

A measurably slow change in nitric acid cannot depend only on proton transfers, which are instantaneous in oxy-acids. Moreover, a slow, and therefore activated, process must involve the breaking of a bond. The orientation laws for nitration, and the effects of substitution on aromatic reactivity in competitive nitration, clearly establish that nitration is an electrophilic substitution. Hence the bond fission must be heterolytic, not homolytic; and hence, also, it must take such a direction as will yield an electrophilic nitrating agent—an entity having the appropriate atomic grouping with an electron-deficient nitrogen atom. Disregarding for the moment, as an easily adjustable detail, the distribution of instantaneously transferable protons, the fundamental heterolysis, the kinetic effect of which stands isolated in zeroth-order nitration, can only be the following:

$$O_2N\overset{|}{-}OH \longrightarrow O_2N^+ + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The active product for nitration is the *nitronium ion*, NO_2^+, and the heterolysis which yields it is clearly analogous to the heterolysis which, in the chemistry of alkyl compounds, gives the alkyl cation, and stands kinetically isolated in unimolecular nucleophilic substitution and elimination. Our kinetic result is a demonstration, jointly, of the *formation and effectiveness of the nitronium ion*. Further demonstrations of its formation will be given in other papers of this group.

The idea that, in certain conditions of nitration, the actual nitrating agent might be the nitronium ion was advanced as early as 1903 by Euler (*Annalen*, 1903, **330**, 280). It has since been supported by Euler himself (*Z. angew. Chem.*, 1922, **35**, 580), by Walden (*ibid.*, 1924, **37**, 390), by Ri and Eyring (*J. Chem. Physics*, 1940, **8**, 433), by Price (*Chem. Rev.*, 1941, **29**, 51), by Kharasch and Westheimer (*J. Amer. Chem. Soc.*, 1946, **68**, 1871), by Bennett, Brand, and

Williams (*J.*, 1946, 869), by Norman Jones, Thorn, Lyne, and Taylor (*Nature*, 1947, **159**, 163), and by Norman Jones and Thorn (*Canadian J. Res.*, 1949, *B*, **27**, 580), but for the most part on evidence less direct than that offered in the present group of papers (and, of course, in our earlier summarising publications, *viz.*, *Nature*, 1946, **158**, 448, 480, 514). A fuller account of the history will be found in a recent article by Gillespie and Millen (*Quart. Reviews*, 1948, **2**, 277).

(1.2.2) *Preliminary Consideration of the Initial Proton Transfer.*—We shall allow our discussion of the proton transfers, which require to be associated with the above fundamental heterolytic process for the purpose of completing a representation of the reactions involved in the formation of the nitronium ion, to rest temporarily on general chemical arguments, reserving a more specific demonstration on the matter for treatment in Section (2.4.1) of this paper.

Consider the following analogy. In the formation of an alkyl cation from an alcohol in strongly acid conditions, a proton uptake certainly precedes heterolysis. This is shown by the acid catalysis of those substitutions, olefin eliminations, and Wagner rearrangements of which the starting substances are alcohols. The heterolysis leading to R^+ thus takes place, not in ROH itself, but in the alkyloxonium ion $R{\cdot}OH_2^+$, doubtless because the group $-OH_2^+$ attracts electrons much more strongly than the group $-OH$. We shall almost certainly be correct if we assume that, analogously, a proton uptake precedes the formation of the nitronium ion, the actual heterolysis taking place, not in the nitric acid molecule itself, but in the derived oxonium cation. The heterolysis of system (10) must be much more facile than that of system (9), and thus it is highly plausible that equation (10) should represent the actual route by which the nitronium ion is produced :

$$O_2NOH_2^+ \longrightarrow O_2N^+ + OH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The reactive entity on the left of this equation is a form of the nitric acidium ion, $H_2NO_3^+$. It may not be the most prevalent form, which possibly has a more evenly distributed arrangement of the protons; but all the prototropic forms will be in mobile equilibrium, owing to the rapidity of proton migrations in oxy-acids; and the form represented above will certainly be that most prone to the particular heterolysis which yields the nitronium ion.

The proton which adds itself to a nitric acid molecule must be expected to come chiefly from the strongest acid present in sufficient quantity in the system. Hence the nature of the main process of proton transfer will be different according as there is, or is not, in the solution an acid which is stronger than nitric acid itself. Perchloric acid, sulphuric acid, and selenic acid are all stronger acids than nitric acid; and in the presence of a very strong acid, such as any of these, we may expect equilibria of the kind illustrated in equations (11) in the example of sulphuric acid:

$$\left.\begin{aligned} HNO_3 + H_2SO_4 &\rightleftharpoons H_2NO_3^+ + HSO_4^- \\ H_2NO_3^+ &\rightleftharpoons NO_2^+ + H_2O \\ H_2O + H_2SO_4 &\rightleftharpoons H_3O^+ + HSO_4^- \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

On the other hand, in the absence of any acid stronger than nitric acid, the latter will itself take on the role of proton donor; and the resulting equilibria will be as follows :

$$\left.\begin{aligned} HNO_3 + HNO_3 &\rightleftharpoons H_2NO_3^+ + NO_3^- \\ H_2NO_3^+ &\rightleftharpoons NO_2^+ + H_2O \\ H_2O + HNO_3 &\rightleftharpoons HNO_3{,}H_2O \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Equations (12) take into account the known fact that no transfer of protons occurs on any considerable scale from nitric acid to small concentrations of water, and that, with nitric acid in large excess, the water forms a hydrogen-bond complex of considerable stability (Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722; cf. Gillespie and Millen, *loc. cit.*, p. 277).

It has been shown that, in sulphuric acid, nitration is of the second order, that in nitric acid it is of the first order, and that in organic solvents it is still of the first order if the aromatic compound is sufficiently unreactive, but of zeroth order if the aromatic compound is sufficiently reactive. It has been made clear that the first three of these results could be accommodated to many theories of nitration, but that the fourth is sharply diagnostic of a preliminary heterolysis to the nitronium ion. However, the first three results are consistent with the same theory provided that due account is taken of the relative rates of formation and destruction of the nitronium ion in the different conditions.

In sulphuric acid, the nitronium ion is formed quickly and completely. Physical evidence concerning this is presented in accompanying papers (*J.*, 1950, papers nos. 499 and 500). The second-order kinetics of nitration in sulphuric acid are a necessary consequence of this situation.

In nitric acid, the nitronium ion is still formed rapidly, but now only in small equilibrium concentration. This can be estimated in various ways to be of the order of 1%, as is shown in Section (2.4.2) of this paper, and in accompanying papers (*J.*, 1950, papers nos. 504 and 510). It follows that the concentration of nitronium ion will remain constant during nitration in nitric acid, and that the reaction will thus exhibit first-order kinetics. In organic solvents, with nitric acid in constant excess, the situation is essentially the same so far as concerns the nitration of sufficiently unreactive aromatic compounds; for even though the small equilibrium concentration of nitronium ion may now be established much more slowly than before, the rate of its establishment is still, by the use of a sufficiently unreactive aromatic compound, rendered much larger than the rate at which the formed nitronium ion is consumed by the aromatic compound. Once again, the nitronium ion will be present in a stationary concentration, closely approximating to its equilibrium concentration, and first-order kinetics will result. But if, in those organic solvents in which the nitronium ion is only slowly formed, we nitrate a sufficiently reactive aromatic compound, this will immediately combine with the nitronium ion as the latter is produced. It follows that the rate of nitration will be equal to the rate of production of the nitronium ion, and this will be constant, if the nitric acid is in constant excess: thus the nitration will be of zeroth order.

(1.2.3) *Preliminary Consideration of the Nitration by the Nitronium Ion.*—The consideration of this process involves another problem concerning proton movements, which we shall here discuss in an introductory manner in preparation for the more careful treatment to be given in Section (3.2). Two main types of mechanism are conceivable, which are as follows.

The first possibility is that, very quickly after the uptake of the nitronium ion, the aromatic proton is ejected into the solvent, there to be passed from molecule to molecule until it, or some proton displaced by it, eventually reaches its most stable situation in combination with the strongest available base. This is a two-stage process, of which the first stage is rate-determining. We may represent it by means of equation (13), calling it "bimolecular" since two original molecules are undergoing covalency change in the transition state of reaction:

$$\left.\begin{array}{l} NO_2^+ + ArH \xrightarrow{\text{slow}} \overset{+}{Ar}\!\!\begin{array}{l}H\\NO_2\end{array} \\ \overset{+}{Ar}\!\!\begin{array}{l}H\\NO_2\end{array} \xrightarrow{\text{fast}} ArNO_2 + H^+ \end{array}\right\} \quad \ldots\ldots\ldots \quad (13)$$

In this mechanism the proton-loss has no kinetic significance: and there is no acceleration of the reaction by solute bases.

The second possibility may be developed from the same formulæ by regarding the first reaction as rapid and rapidly reversible, and by assuming that the resulting pre-equilibrium is followed by a slow, and therefore rate-determining, extraction of the aromatic proton by some sufficiently powerful base. Such a reaction may be called "termolecular": whether the transition state is built up by successive bimolecular encounters, or by a single termolecular encounter, it will contain three original species all undergoing covalency change, *viz.*, the nitronium ion, the aromatic molecule, and the necessary base (which might, *e.g.*, be a hydrogen sulphate, or a nitrate ion). Writing B^- for the base, this mechanism may, for all kinetic purposes, be expressed by the single equation (14):

$$NO_2^+ + ArH + B^- \longrightarrow NO_2Ar + HB \quad \ldots\ldots\ldots \quad (14)$$

This process is evidently base-accelerated; and the proton-loss has in this case definite kinetic importance.

We shall later develop the thesis that for nitration by nitric acid in sulphuric acid, nitric acid, nitromethane, and acetic acid solvents, the "bimolecular" mechanism (13) prevails (cf. Section 3).

(Discussion continued on p. 2419.)

(2) Solute Effects on Nitration Kinetics: Mechanism of Formation of the Nitronium Ion.

(2.0) *Significance of the Kinetic Effects of Solutes.*—This Section brings together our work on the kinetic effects produced by three added substances in particular, *viz.*, sulphuric acid, potassium nitrate, and water. The reason for collectively treating the kinetic effects of these three solutes is that it is through their study that we have sought for evidence concerning the

nature of the reactions by which the nitronium ion is formed, on which nitration has been shown to depend. We may expect in this way to discover at what stage proton transfers enter into the process, at what stage nitrate ion appears in the sequence of changes, and at what stage water is produced, or, alternatively, such products as water would give by interaction with the medium; and from this information we may expect to be able to reconstruct the sequence of reactions. Following the presentation of our results on the solute effects mentioned, a discussion will be given along these lines.

There is a fourth solute the kinetic effects of which have been studied in some detail, *viz.*, nitrous acid. Because this work tends in a different direction, it is described and discussed in a later Section. The principal unknown here was the constitution of the nitrous acid, and it is mainly on this problem that the kinetic evidence bears.

(2.1) *Observations on the Kinetic Effects of Sulphuric Acid.*

(2.1.1) *Effect of Added Sulphuric Acid on Zeroth-order Rates of Nitration.*—Except for nitration in very strongly acidic solvents, such as sulphuric acid, and nitration in basic solvents such as water, the rule is general that small concentrations of added very strong acids, such as perchloric acid, sulphuric acid, or selenic acid, greatly increase rates of nitration. We have investigated this phenomenon quantitatively in the example of added sulphuric acid, treating both zeroth-order and first-order reactions.

Small concentrations of added sulphuric acid strongly accelerate zeroth-order nitrations, without detectably disturbing their zeroth-order form, within the range of our observations. This has been established for the nitrations of benzene and toluene in nitromethane as solvent, with several concentrations of nitric acid, and in the presence of various amounts of nitrous acid. The observed forms of acceleration are somewhat dependent on the proportion of nitrous acid present. Such forms are illustrated by reference to two series of experiments in Table VI. The rate constants of the first series are plotted as a function of the concentration of the added sulphuric acid in Fig. 7.

TABLE VI.

Effects of added sulphuric acid on zeroth-order rate constants (k_0 *in sec.*$^{-1}$ *g.-mol.l.*$^{-1}$) *for nitrations by nitric acid in nitromethane.*

$[HNO_3] = 3{\cdot}0$M. Temp. $= -10{\cdot}0°$.

Expt.	HAr.	$[HAr]_0$.	$[HNO_3]_0$.	$[H_2SO_4]_0$.	10^4k_0.	Expt.	HAr.	$[HAr]_0$.	$[HNO_3]_0$.	$[H_2SO_4]_0$.	10^4k_0.
				Series A :							
230	PhH	0·115	0·0034	none	0·103	236	PhH	0·115	0·0034	0·0329	4·71
235	,,	,,	,,	,,	0·104	233	,,	,,	,,	0·0424	6·38
231	,,	,,	,,	0·0053	1·65	232	,,	,,	,,	0·0452	6·33
234	,,	,,	,,	0·0206	3·10						
				Series B :							
242	PhMe	0·150	0·0793	none	0·053	245	PhMe	0·150	0·0793	0·0631	1·41
244	,,	,,	,,	0·0144	0·128	246	,,	,,	,,	0·0842	1·86
243	,,	,,	,,	0·0418	0·712						

When the nitrous acid is present in quantities greater than, or about equal to, the quantity of added sulphuric acid, it notably reduces the accelerative effect of the latter. This can be seen by comparing the rate constants of Series B in Table VI with those of Series A. It would appear that nitrous acid, if not too dilute, is able largely to destroy the catalytic effect of an amount of sulphuric acid comparable to its own amount. However, nitrous acid, when present in quite dilute solution, and in quantities considerably smaller than the quantities of added sulphuric acid, has no significant influence on the kinetic effect of the latter; and it is in these conditions that the linear relation appears, which is illustrated in Fig. 7. Although the quantity of nitrous acid, in the experiments here represented, is too small seriously to influence the rates obtained in the presence of sulphuric acid, it is sufficient to reduce the rates in the comparison experiments without added sulphuric acid by about one-third. However these rates are so small in comparison with the catalysed rates that the effect mentioned does not upset the general linearity shown.

A similar plot of the results of Series B would furnish a curve, which, as compared with the curve of Fig. 7, is much more nearly horizontal, and is distinctly concave to the rate axis. This illustrates the effect of increasing the concentration of nitrous acid. It can be understood on the basis that nitrous acid inactivates a certain amount of sulphuric acid by reacting with it, nearly completely when the acid is in deficit, but only partly when the acid is in excess.

Therefore we take the most significant result of these experiments to be the linear catalysis illustrated by Series A. Two factors probably contribute to the simplicity of the result: one is that the concentration of added sulphuric acid is small; and the other is that the total catalytic effect is large, *i.e.*, that the catalysed rates are many times larger than the uncatalysed.

The sensitivity of the reaction to catalysis by sulphuric acid may be specified by stating that a 0·001M-concentration of the acid doubles the rate. This figure assumes the absence of disturbances by nitrous acid, a correction having been applied for the effect of nitrous acid on the rate of the uncatalysed reaction in the experiments of Series A.

(2.1.2) ***Effect of Added Sulphuric Acid on First-order Rates of Nitration.***—Like zeroth-order nitrations in nitromethane, first-order nitrations are accelerated notably by small concentrations of added sulphuric acid, without detectable disturbance to the kinetic form of the reaction. It has been found that in all qualitative respects the effect of sulphuric acid on first-order reactions is closely parallel to its effect on zeroth-order reactions under similar conditions.

Considerable quantitative differences appear in the effect as it applies to first-order nitrations with nitric acid as both solvent and reagent. In these conditions there are no known zeroth-order reactions for comparison. In illustration of the effect, we give in Table VII a series of first-order rate constants for the nitration of 1-nitroanthraquinone in nitric acid, with and without added sulphuric acid.

FIG. 7.

Effect of sulphuric acid on zeroth-order nitration rates: nitration of benzene by 3M*-nitric acid in nitromethane at* −10·0°.

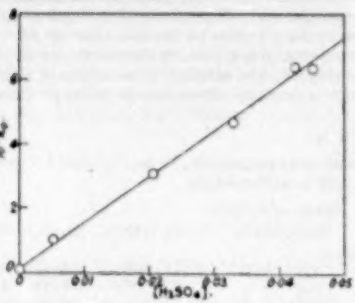


FIG. 8.

Effect of sulphuric acid on first-order nitration rates: nitration of 1*-nitroanthraquinone in nitric acid at* 20·0°.

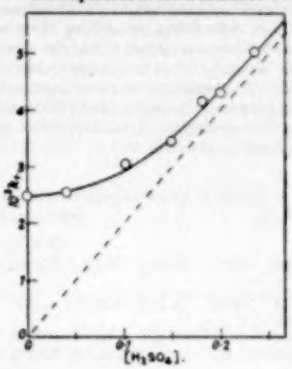


TABLE VII.

Effect of added sulphuric acid on first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of* 1*-nitroanthraquinone in nitric acid at* 20·0°.

Expt.	$[C_{14}H_7O_4N]_0$.	$[HNO_3]$.	$[H_2SO_4]$.	10^4k_1.	Expt.	$[C_{14}H_7O_4N]_0$.	$[HNO_3]$.	$[H_2SO_4]$.	10^4k_1.
371	0·0241	0·0055	none	248	375	0·0238	0·0065	0·176	419
372	0·0263	0·0085	0·044	283	376	0·0255	0·0150	0·201	431
373	0·0252	0·0090	0·101	309	377	0·0260	0·0070	0·234	503
374	0·0252	0·0097	0·147	343					

In these experiments the influence of nitrous acid is small enough to be neglected. A plot of the rate constants against the concentration of sulphuric acid is shown in Fig. 8. Evidently, added sulphuric acid accelerates the reaction. But in proportion to the uncatalysed rate, the observed accelerations are much smaller than those found for nitrations in nitromethane, when in this solvent effects of nitrous acid may be neglected. In particular, the concentration of sulphuric acid which is required in order to double the rate in nitric acid is 0·23M., *i.e.*, it is about 200 times greater than in the experiments in nitromethane already quoted.

As Fig. 8 shows, the accelerations observed in solvent nitric acid are far from linear. The sensitivity of the reaction to the catalysis is small at low catalyst concentrations, but it rises as the concentration of sulphuric acid increases. In the upper part of the investigated range of

concentrations, we find some approach to linear acceleration, and this leads us to think that the form of the catalysis in nitric acid is not different in principle from the form observed in nitromethane. We assume that, if the curve of Fig. 8 could be continued, without losing simplifying effects due to the dilution of the sulphuric acid, until the catalysed reaction were many times faster than the uncatalysed, then the total curve would be linear over nearly all its length, like the curve in Fig. 7; and that, if the magnified lower extremity of the curve of Fig. 7 could be investigated sufficiently minutely, it would be found to turn before meeting the rate axis, like the curve of Fig. 8. We shall discuss these assumed relationships later [Section (2.4.2)].

(2.2) *Observations on the Kinetic Effects of Nitrates.*

(2.2.1) *The General Salt Effect and the Specific Nitrate Ion Effect.*—Exploratory experiments have shown that an appreciable general salt effect influences both zeroth- and first-order nitration in nitromethane. The effect is exerted typically by the alkali-metal salts of very strong acids—salts such as potassium perchlorate and potassium hydrogen sulphate. The effect is accelerative, as we should expect if it be a primary salt effect, bearing in mind the general parallelism between primary salt effects and solvent effects, and the known direction of the solvent influence on nitration rate. However, this salt effect is small; in particular, it is small enough to be neglected in comparison with the specific salt effect next to be mentioned.

The specific effect has been established for a number of alkali-metal and ammonium nitrates. It consists in a strong negative catalysis. It has been observed to influence both zeroth-order and first-order nitrations, without detectably disturbing the kinetic form of either. This anticatalytic behaviour seems to be specific to nitrates; and the cation of the salt appears to have very little concern with the effect, which we presume to originate in the nitrate ion itself.

Data for some of the exploratory runs are given in Table VIII: they refer to the zeroth-order nitration of toluene in nitromethane. Though the disturbances caused by the nitrous acid are not inappreciable, the figures given suffice to show the direction and relative magnitude of the two salt effects. They show, for instance, that whilst the increase of rate produced by 0·01M-potassium perchlorate is only just detectable, a similar concentration of lithium or potassium nitrate will reduce nitration rate by factors of the order of one-half.

TABLE VIII.

Effects of certain salts on the zeroth-order rate constants (k_0 *in sec.*$^{-1}$ *g.-mol.l.*$^{-1}$) *of nitration of toluene in nitromethane.*

$[HNO_3] = 7{\cdot}0$M. Temp. $= -10{\cdot}0°$.

Expt.	$[HNO_3]_0$.	$[C_7H_8]_0$.	Salt.	[Salt].	10^4k_0.	Expt.	$[HNO_3]_0$.	$[C_7H_8]_0$.	Salt.	[Salt].	10^4k_0.
202	0·0046	0·100	none	—	9·78	206	0·0043	0·093	$LiNO_3$	0·0084	6·02
204	,,	,,	$KClO_4$	0·0107	10·30	212	0·0070	,,	KNO_3	0·0123	4·30
207	,,	,,	KNO_3	0·0065	6·58						

In the course of our work on the kinetics of nitration in acetic acid, we made an attempt to eliminate the disturbing effect of nitrous acid by the addition of urea. Since nitrous acid depresses nitration rates, the expectation was that the addition of urea would lead to a larger rate. Actually it led to a smaller rate, as is shown in Table IX. We concluded that urea nitrate was producing an anticatalytic effect stronger than that of the original nitrous acid. It was clear that the effect must be powerful, because urea nitrate is only slightly soluble in acetic acid. We assume the effect to be due to the nitrate ion.

TABLE IX.

Effect of urea nitrate on first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of benzene in acetic acid.*

Expt.	$[HNO_3]_0$.	$[HNO_2]_0$.	$[C_6H_6]_0$.	Temp.	$CH_5O_4N_3$.	10^4k_1.
401	7·8	0·0013	0·10	0·0°	none	37·9
400	,,	none	,,	,,	saturated	18·1

Acetic acid is a poor solvent for alkali-metal nitrates. In the more detailed study of the nitrate-ion effect now to be described, we therefore investigated nitration in nitromethane, or in nitric acid itself, finding them more convenient than acetic acid as solvents for the salts employed.

(2.2.2) *Effect of Added Potassium Nitrate on Zeroth-order Rates of Nitration.*—The form of the effect of added potassium nitrate on the rate of a zeroth-order nitration may be illustrated by the block of experiments recorded in Table X, which relates to the nitration of toluene by

7M-nitric acid in nitromethane. The disturbances caused by the small amounts of nitrous acid, which were present in the solutions, are negligible in relation to the effect under observation. The anticatalytic effect of the potassium nitrate is evidently powerful, a 0·004M-concentration being sufficient to halve the reaction rate.

TABLE X.

Effect of added potassium nitrate on the zeroth-order rate constants (k_0 *in sec.*$^{-1}$*g.-mol.l.*$^{-1}$) *for the nitration of toluene in nitromethane.*

$[HNO_3]$ = 7·0M. $[HNO_3]$ = 0·0013—0·0024M. (extreme values).
$[C_7H_8]_0$ = 0·09M. Temp. = −10·0°.

Expt.	$[KNO_3]$.	10^4k_0.	Expt.	$[KNO_3]$.	10^4k_0.	Expt.	$[KNO_3]$.	10^4k_0.
581	none	3·95	584	0·02312	2·18	587	0·1124	1·57
591	"	3·85	585	0·02702	2·23	588	0·2799	1·30
582	0·00346	4·78	586	0·04306	1·87	589	0·6302	0·94
583	0·00587	3·89						

A plot of the reciprocal of the rate against the concentration of the added salt is shown in Fig. 9. The reason for choosing this particular form of graphical representation will be

FIG. 9.

Effect of potassium nitrate on zeroth-order rates of nitration of toluene by 7M-nitric acid in nitromethane at −10·0°.

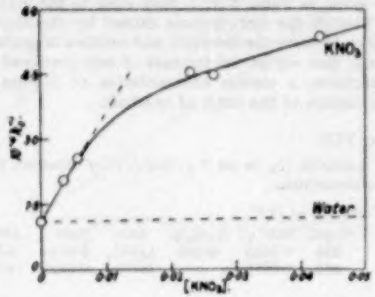
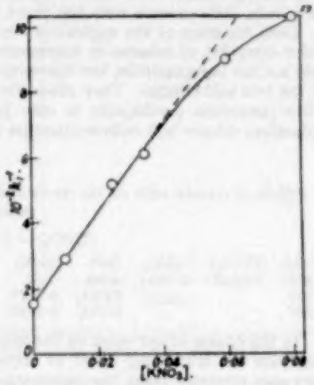


FIG. 10.

Effect of potassium nitrate on first-order rates of nitration of p-dichlorobenzene by 8·5M-nitric acid in nitromethane at 20·0°.



explained later. The results are consistent with the idea, to which other groups of experiments point more definitely, that in the low concentration range the effect of the added salt on the reciprocal of the rate is asymptotically linear.

Added water is well known to reduce nitration rates. The broken line near the bottom of the diagram represents the effect of replacing the added potassium nitrate by its molecular equivalent of added water. It will be seen how much more sensitive the rate is to potassium nitrate than it is to water. We shall return to this point later [Section (2.4.1)].

(2.2.3) *Effect of Added Potassium Nitrate on First-order Rates of Nitration.*—The form of the effect of added potassium nitrate on the rate of a first-order nitration is illustrated by the block of experiments recorded in Table XI. They relate to the nitration of *p*-dichlorobenzene by

TABLE XI.

Effect of added potassium nitrate on the first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of* p-*dichlorobenzene in nitromethane.*

$[HNO_3]$ = 8·5M. $[H_2O]_0$ = 0·3M. $[C_6H_4Cl_2]_0$ = 0·10M. $[HNO_3]$ = 0·008M. Temp. = 20·0°.

Expt.	$[KNO_3]$	10^4k_1.	Expt.	$[KNO_3]$	10^4k_1.	Expt.	$[KNO_3]$	10^4k_1.
301	none	649	303	0·0250	193	306	0·0606	111
307	0·0160	348	302	0·0349	164	305	0·0809	97

means of 8·5M-nitric acid in nitromethane. The disturbance caused by the nitrous acid present in these experiments is negligible in relation to the effect under observation.

The relation between the reciprocal of the first-order rate constant and the concentration of the salt is shown graphically in Fig. 10. The result is somewhat similar to that obtained in the corresponding representation of zeroth-order rates shown in Fig. 9; but there are two differences. For the first-order reactions, the linear relation between the reciprocal of the rate-constant and the concentration of the salt holds up to a larger salt concentration, *viz.*, 0·05M. Also the sensitivity of the first-order reactions to the effect of nitrates is smaller, a salt concentration of 0·01M. being needed to halve the rate constant.

When the concentration of the nitric acid is increased until the acid is essentially the solvent as well as the nitrating agent, the nitration rates are still reduced by added potassium nitrate,

FIG. 11.

Effect of potassium nitrate in first-order rates of nitration of nitrobenzene in nitric acid at 0·0°.

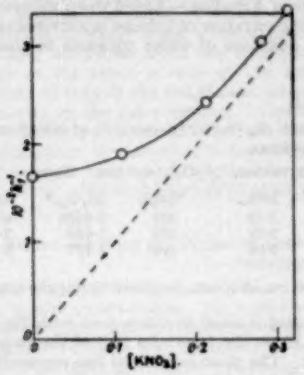
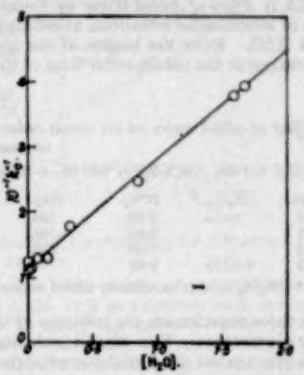


FIG. 12.

Effect of water on zeroth-order rate of nitration of toluene by 7M-nitric acid in nitromethane at −10·0°.



but the quantitative aspect of the effect is changed. Some data referring to first-order nitrations of nitrobenzene in nitric acid are given in Table XII.

TABLE XII.

Effect of added potassium nitrate on first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of nitrobenzene in nitric acid.*

$[H_2O]_0 = 2·5$M. $[HNO_3] = 0·02$M. $[C_6H_5O_2N]_0 = 0·215$M. Temp. = 0·0°.

Expt.	$[KNO_3]$.	10^3k_1.	Expt.	$[KNO_3]$.	10^3k_1.	Expt.	$[KNO_3]$.	10^3k_1.
215	none	607	217	0·110	530	603	0·282	328
601	,,	597	602	0·114	533	604	0·315	296
218	,,	595	219	0·214	411			

In these experiments the influence of nitrous acid is negligible in comparison with that of potassium nitrate. This effect is, however, smaller by factors up to 80 than those shown in the preceding illustrations, a salt concentration of 0·31M. now being necessary in order to halve the first-order rate constant. Moreover, as Fig. 11 shows, the plot of the reciprocal of the rate constant against the concentration of potassium nitrate is far from linear in the low concentration range, although it seems to become asymptotically linear at the higher salt concentrations.

There are obvious resemblances between this reciprocal-rate curve for the anticatalytic effect of potassium nitrate, and the rate curve of Fig. 8 for the catalytic effect of sulphuric acid, on nitration in nitric acid. It is probably not accidental that the reciprocal-rate curve of Fig. 11 turns to meet the reciprocal-rate axis in the same concentration range as that in which the rate curve of Fig. 8 turns to meet the rate axis; that both curves converge towards straight lines through the origin in the higher concentration region; and that the concentration of

anticatalyst required to halve the rate of the anticatalysed reaction is nearly the same as the concentration of catalyst necessary to double the rate of the catalysed reaction.

In nitromethane solution also close similarities can be found between the effect of potassium nitrate on the reciprocal of the rate of nitration and that of sulphuric acid on the rate of nitration. Both effects apply to zeroth-order and first-order reactions alike, without disturbance to the reaction order; both effects have certain ranges of linearity; and both decrease in intensity with increasing concentration of nitric acid. At a given concentration of nitric acid, the concentration of potassium nitrate required to halve the rate of nitration is always of the same order of magnitude as the concentration of sulphuric acid needed to double the rate of the same nitration. Thus the necessary concentrations of potassium nitrate or of sulphuric acid increase by similar factors, each about $10^{\frac{1}{2}}$, as the concentration is increased from the lowest employed in these experiments, *viz.*, 7M., up to that of pure nitric acid, *viz.*, 24M. These analogies will be discussed later [Section (2.4.2)].

(2.3) *Observations on the Kinetic Effects of Water.*

(2.3.1) *Effect of Added Water on Zeroth-order Rates of Nitration.*—Added water depresses the rates of zeroth-order nitrations, as is illustrated, for the nitration of toluene in nitromethane, in Table XIII. Even the largest of the investigated additions of water appeared to create no disturbance in the zeroth-order form of the reaction.

TABLE XIII.

Effect of added water on the zeroth-order rate constants (k_0 *in sec.*$^{-1}$*g.-mol.l.*$^{-1}$) *of nitration of toluene in nitromethane.*

$[HNO_3] = 7{\cdot}0$M. $[HNO_3] = 0{\cdot}0013$—$0{\cdot}0024$M. (extreme values). $[C_7H_8]_0 = 0{\cdot}09$M. Temp. $-10{\cdot}0°$.

Expt.	$[H_2O]_0$.*	10^4k_0.	Expt.	$[H_2O]_0$.*	10^4k_0.	Expt.	$[H_2O]_0$.*	10^4k_0.
581	none	8·93	594	0·0809	7·76	597	0·8589	4·11
591	,,	8·85	595	0·1633	7·72	598	1·586	2·61
592	,,	7·97	596	0·3122	5·56	599	1·677	2·53
593	0·0179	8·61						

* $[H_2O]_0$ relates to initially added water: extra water is, of course, produced during the nitration.

In these experiments the influence of the nitrous acid is small in comparison with the effect under observation. This effect is exhibited in Fig. 12, in the form of a plot of the reciprocal of the rate against the initial concentration of water. The short horizontal line represents the approximate amount of extra water which is produced during the runs. If in the construction of the graph we had used average, instead of initial, water concentrations, all the points, and the line drawn through them, would have been shifted to the right by half this length. This would not affect the conclusion that the reciprocal of the rate is a linear function of the concentration of the water.

The anticatalytic effect of water is evidently very weak in comparison with that of nitrate ions. Thus a concentration of 0·6M. of added water is required to halve the rate of this reaction, whereas the same can be done by a concentration of only 0·004M. of added potassium nitrate. The line representing the water effect in Fig. 12 was reproduced on the appropriate scale in Fig. 9, for comparison with the graph there shown of the nitrate ion effect.

(2.3.2) *Effect of Added Water on First-order Rates of Nitration.*—Added water exerts a retarding influence also on first-order rates of nitration; and it does this without detectably disturbing the kinetic order of the reaction. This effect is illustrated with reference to the nitration of nitrobenzene in pure nitric acid, with and without added water, by the figures in Table XIV.

TABLE XIV.

Effect of added water on the first-order rate constants (k_1 *in sec.*$^{-1}$) *of nitration of nitrobenzene in nitric acid.*

$[C_6H_5O_2N]_0 = 0{\cdot}07$—$0{\cdot}12$M. (extreme values). $[HNO_3] = 0{\cdot}040$M. Temp. $= -13{\cdot}3°$.

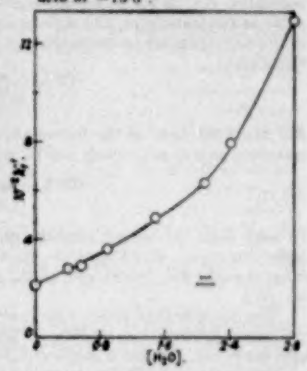
Expt.	$[H_2O]_0$.*	10^4k_1.	Expt.	$[H_2O]_0$.*	10^4k_1.	Expt.	$[H_2O]_0$.*	10^4k_1.
400	none	468	401	0·891	276	406	2·42	125
405	0·396	354	403	1·45	204	407	3·19	77
402	0·557	341	404	2·10	157			

* $[H_2O]_0$ relates to water initially added to pure nitric acid, which at $T°$ c. has the density $1{\cdot}5360 - 0{\cdot}0014T$, and is therefore 24·58M. at $-13{\cdot}3°$.

The kinetic influence of the nitrous acid present in these experiments is negligible in relation to the effect under observation. This effect of the water is shown graphically in Fig. 13, which exhibits a plot of the reciprocal of the rate constant against the concentration of added water. The amounts of extra water produced by nitration are indicated, as lower and upper limits, by the two short, horizontal lines on the diagram. In a corresponding graph relating to average, instead of to initial, water concentrations, the points would be shifted to the right of the points shown by distances within the range of the half-lengths of these two lines.

FIG. 13.

Effect of water on first-order rate of nitration of nitrobenzene in nitric acid at −13·3°.



We have not been able to find any simple function of obvious chemical significance to fit this curve, which appears to steepen continuously as the water concentration increases. It does so especially rapidly at concentrations around 2·2M., which, as we shall notice later [Section (2.4.2)], is critical in another connexion.

The anticatalytic effect of water on nitration in nitric acid is evidently weak, a water concentration of 1·2M. being needed to halve the rate constant. The intensity of the effect is thus of the same order of magnitude as that of the retardation caused by potassium nitrate in the same medium. This similarity of magnitude forms a contrast to the quite different orders of magnitude of the retarding influences of water and nitrate ions, as they affect zeroth-order nitrations in nitromethane. We shall comment on this later [Section (2.4.2)].

(2.4) *Discussion (Part 2) : Effects of Some Solutes : Mode of Formation of the Nitronium Ion* **(continued from p. 2412).**

(2.4.1) *Effects of Strong Acids, Nitrates, and Water : The Nitric Acidium Ion.*—The following results require consideration. (1) Added very strong acids, such as sulphuric acid, accelerate both zeroth-order and first-order nitration, without changing the reaction order, the rate varying nearly linearly with the concentration of the added acid within certain ranges (cf. Figs. 7 and 8). The effect is strong for nitrations in nitromethane, but much weaker for nitrations in nitric acid; and in the latter case considerable deviations from linearity occur at low concentrations of added acid. (2) Added nitrates, such as potassium nitrate, retard both zeroth-order and first-order nitrations, without changing the kinetic form, the reciprocal of the rate varying nearly linearly with the concentration of the added nitrate within certain ranges (cf. Figs. 9, 10, and 11). The effect is strong for nitrations in nitromethane, but much weaker for nitrations in nitric acid. In the former case deviations from linearity set in at the higher concentrations of nitrate, whilst in the latter the chief deviations occur at the lower concentrations of added nitrate. (3) Added water retards both zeroth-order and first-order nitrations, without changing the reaction order, the reciprocal of the rate varying nearly linearly with the concentration of water, within certain ranges (cf. Figs. 12 and 13). In comparison with the strong effects already mentioned, the effect of water is weak, as well for zeroth-order nitrations in nitromethane as for first-order nitrations in nitric acid. In the latter case marked deviations from linearity appear.

From these results we first select for consideration the strong effects, which most plainly indicate the general character of the interpretation. These effects are the acceleration by very strong acids, and the retardation by nitrates, of nitrations in nitromethane, always without disturbance to the reaction order. The accelerations show that a proton uptake by nitric acid is necessary to the formation of the nitronium ion. The retardations show that a nitrate ion is eliminated in a reaction leading to the nitronium ion, and that the reaction in which it is eliminated can be driven backwards by added nitrate ion.

One of these strong effects is particularly significant : it is that zeroth-order nitration is strongly retarded by nitrate ion, *without losing its zeroth-order character*. This immediately shows that the formation of the nitronium ion, which is the rate-determining stage of zeroth-order nitration, itself consists of two stages; for some reaction-stage in the production of the nitronium ion, namely, the stage in which a nitrate ion is eliminated, must be reversible. But

another stage, namely, the final stage in the production of the nitronium ion must be effectively irreversible; for the essence of the interpretation of zeroth-order nitration is that none of the formed nitronium ion goes back into what it came from, all being consumed in the nitration of the aromatic compound. If we should try strongly to depress nitration rate by reversing the formation of the nitronium ion, we should inevitably convert a zeroth-order reaction into a first-order reaction.

These few facts thus determine the mechanisms written below for the formation of the nitronium ion, as measured in zeroth-order nitrations, with or without catalysis by such strong acids as sulphuric acid, and with or without anticatalysis by the nitrate ion. For the formation of the nitronium ion in zeroth-order nitrations catalysed by sulphuric acid, we have the following equations:

$$\left.\begin{aligned} HNO_3 + H_2SO_4 &\rightleftharpoons H_2NO_3^+ + HSO_4^- \\ H_2NO_3^+ &\longrightarrow NO_2^+ + H_2O \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

For the formation of the nitronium ion in the absence of a catalysing acid, we have a corresponding expression, which automatically "takes care" of the retardation by nitrate ion:

$$\left.\begin{aligned} HNO_3 + HNO_3 &\rightleftharpoons H_2NO_3^+ + NO_3^- \\ H_2NO_3^+ &\longrightarrow NO_2^+ + H_2O \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In each case, the second reaction-stage is expressed irreversibly, as is appropriate to zeroth-order nitration. For simplicity, the formed water is shown as free water, though we know that it becomes largely linked with nitric acid as the hydrate of nitric acid (cf. Gillespie and Millen, *loc. cit.*).

The observations cited thus provide the first definite demonstration of the formation of the *nitric acidium ion*, $H_2NO_3^+$. They show at the same time that, side by side with the nitronium ion, this ion is ineffective for nitration in the conditions investigated.

Equations (15) and (16) represent the rate of formation of the nitronium ion, *i.e.*, the zeroth-order nitration rate, as proportional to the equilibrium concentration of the nitric acidium ion. Thus the equations require, given certain simplifying conditions mentioned below, that sulphuric acid should produce a linear increase of rate, and that potassium nitrate should bring about a retardation corresponding to a linear increase in the reciprocal of the rate. The fact that we find such linear effects in certain ranges, and no signs of the corresponding quadratic effects, shows that only one proton is absorbed into, and only one nitrate ion is eliminated from, the system out of which the nitronium ion is directly generated. Thus the cation involved in the pre-equilibrium is $H_2NO_3^+$, as represented, and is not $H_2NO_3^{++}$; for the formation of this bivalent ion would involve the intake of two protons and the elimination of two nitrate ions, and therefore should lead to quadratic, rather than the linear, catalytic and anticatalytic effects.

An obvious condition for linearity of the catalysis by sulphuric acid is that the process by which the nitronium ion is formed should essentially be that of equations (15) only, not a mixture of the processes of equations (15) and (16) in comparable proportions. This condition will be fulfilled if, as in our experiments on catalysed zeroth-order nitration, the catalysis is strong, *i.e.*, if the catalysed rate is many times larger than the uncatalysed rate. A necessary condition for the expected linear effect in the anticatalysis by potassium nitrate is that the salt should be fully dissociated into ions having the normal type of activity coefficient; and it is to the failure of this condition in nitromethane that we attribute the marked falling off in the specific anticatalytic effect of the salt at the higher concentrations investigated.

In the approximation to which the above treatment is carried, added water has no effect on zeroth-order nitrations; that is, it has no kinetic effect comparable in magnitude to the effects of strong proton-donors or of nitrates. This is consistent with equations (15) and (16), in which water appears only in the irreversible part of the process: nitrate ion is formed, but no water is formed, in the one reaction-stage which, in zeroth-order nitration, can be driven backwards.

However, when we begin to take account of the finer details of the experimental investigation, we have to deal with the position that added water does depress the rate, although its specific kinetic effect is some hundreds of times smaller than those of nitrates or strong acids. This effect is not due to a small reversibility of the second reaction-stage expressed in equations (16); for by adding enough water, we can reduce the rate considerably, *e.g.*, to one-third or one-quarter of its original value, without detectably disturbing the zeroth-order form of the reaction. Taking account of this, and also of the observation that the kinetic effect of water is essentially linear with respect to the reciprocal of the rate, we infer the existence of a second

process of destruction of the nitric acidium ion in a reversible reaction—one which is formally similar to, but much less important than, the reversible reaction-stage of equations (16). The chemical nature of this second reversible reaction is determined by the requirement that the products of the forward process must be nitric acidium ion and water. It may be represented as part of an alternative route to the nitronium ion, *viz.*, the following:

$$\left.\begin{array}{l} HNO_3 + H_3O^+ \rightleftharpoons H_2NO_3^+ + H_2O \\ H_2NO_3^+ \longrightarrow NO_2^+ + H_2O \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Here the equilibrium in the first reaction-stage must lie so far over to the right that the water normally formed in the reactions of equations (16) destroys very little of the nitric acidium ion, and thus produces only minute concentrations of hydroxonium ion. But when considerably more water is added to the system, then the reversible stage of process (17) retrogresses to a significant extent, reducing the stationary concentration of the nitric acidium ion, and therefore reducing the rate of formation of the nitronium ion. The linearity of the effect of water on the reciprocal of the rate is evidently accommodated by equations (17).

It will be obvious that, if we should add yet much more water, we must eventually produce a reversal of the second stage of these processes, with the result that zeroth-order kinetics will go over into first-order kinetics. Such a kinetic conversion has not been followed in detail,* though the results of a completed conversion of this type have been studied, as is reported in the next paper (Part III).

In first-order nitration, in contrast to zeroth-order nitration, the re-hydration of the nitronium ion has to be considered as rapid in relation to the reaction of nitronium ion with the aromatic compound. The discussion of these nitrations can therefore be based on a summarised representation of the processes leading to the nitronium ion. In this representation the two stages of each of the processes (15), (16), and (17) are combined, the total process being treated as reversible. Thus, for the reactions catalysed by sulphuric acid, we have the following equilibrium:

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

In the absence of a catalysing acid, the principal equilibrium will be the following, which takes account of the anticatalysis of first-order nitrations by nitrate ions:

$$HNO_3 + HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

There will be another reversible process of some importance in the presence of considerable quantities of water, namely, the following:

$$HNO_3 + H_3O^+ \rightleftharpoons NO_2^+ + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

We are still representing the water as free for simplicity, although we know that in nearly pure nitric acid most of it is combined as a hydrate of the acid.

Since in first-order nitration the nitronium ion is maintained in a stationary concentration, to which the first-order rate constant is proportional, we must expect the first-order constant to be increased linearly by added sulphuric acid, and decreased so that its reciprocal is increased linearly by nitrate ions—always provided that certain simplifying conditions are satisfied. These conditions are the same as for zeroth-order nitration, with the additional requirement that, while the effect of nitrate ion is being studied, the water should be in constant excess. The expected influence of water is rather complicated, partly because an inverse quadratic effect is allowed by equation (20).

As with zeroth-order nitrations, so also with first-order nitrations, the conditions necessary for the production of the linear kinetic relations are most easily satisfied for nitrations in nitromethane. The special requirement for linear anticatalysis by nitrate, *viz.*, that the water should be in constant excess, can also be easily satisfied in this solvent, because such small concentrations of nitrate suffice to produce a substantial kinetic effect. An example showing the linear anticatalysis by potassium nitrate of a first-order nitration under such conditions has been given.

* Since this was written such a conversion has been followed through by Mr. M. H. Jones, with a practical object. He was concerned to compare the nitration rates of toluene and *tert.*-butylbenzene, and, since the use of the competition method would in this case involve a difficult analysis, he turned to the kinetic method, for which, with nitric acid in constant excess, first-order kinetics are essential in this type of experiment. It happens that, in the otherwise convenient solvent acetic acid, both these nitrations have zeroth-order kinetics. Therefore Mr. Jones added progressively increasing quantities of water, up to 5% by weight, to the acetic acid solvent, thereby driving the kinetics over from zeroth order to first order, in accordance with expectation.

Perhaps the main interest attaching to the experiments concerning solute effects on first-order nitrations relates to what happens when the conditions necessary for the linear relations are not fulfilled—as, generally, they are not for nitration in nitric acid itself. We proceed to consider this matter.

(2.4.2) *Further Effects of Acid, Nitrate, and Water: The Self-ionisation of Nitric Acid.*—Most of the non-linear effects which have been observed in connexion with the kinetic influence of these solutes on nitrations with nitric acid as both solvent and reagent can be understood on the basis that pure nitric acid is considerably self-ionised in the sense of equation (19). The self-ionisation is much greater than when the nitric acid is present in organic solvents. The effects to be expected from a substantial self-ionisation are readily deduced.

For example, when, by an addition of sulphuric acid, nitronium ion is produced by reaction (18), the new nitronium ion will destroy some of the old nitronium ion by repressing equilibrium (19): thus the two sources of nitronium ion will not behave additively, and the catalysis will not be linear. But if the added sulphuric acid has generated enough nitronium ion to suppress to insignificance its production in the original equilibrium (19), then the introduction of further quantities of sulphuric acid will yield nearly additive increments of nitronium ion, and so the catalysis will asymptotically become linear. Departures from linearity are marked up to a concentration of sulphuric acid of about 0·2M.; and hence we may conclude that the production of nitronium ion by equilibrium (19), in pure and nearly pure nitric acid, is of the order of 0·2M.

A similar effect arises in anticatalysis by metallic nitrates. The immediate result of the introduction of an ionised nitrate will be to repress equilibrium (19), thus reducing the production of nitrate ions by the original method: hence the two sources of nitrate ions will not operate additively, and the total nitrate ion will not increase linearly with the amount of added nitrate. This means that, even if the water concentration is buffered, as it was in the relevant experiments, the reciprocal of the concentration of nitronium ion, and therefore the reciprocal of the first-order rate constant, will not increase linearly with the added metallic nitrate. Only when the amount of added nitrate is greater by several fold than the amount of nitrate ion originally produced by the self-ionisation, will further additions of nitrate linearly increase the total concentration of nitrate; and only then will the effect of the added nitrate on the reciprocal of the first-order rate constant asymptotically become linear. A consideration of the range of concentrations over which marked deviations from linearity occur in the anticatalytic effect of added nitrate allows us to estimate that the concentration of nitrate ion originally produced by the self-ionisation of nitric acid is of the order of 0·2M. This estimate is consistent with that given above for the concentration of nitronium ion in self-ionised nitric acid, and also with the physical evidence concerning the self-ionisation of nitric acid which is presented in accompanying papers (*J.*, 1950, papers nos. 504, 505).

It seems possible to conclude from the kinetic results that potassium nitrate is fully ionised up to much greater concentrations in nitric acid than it is when nitromethane is the main constituent of the solvent.

The reason for the much smaller sensitivity of nitration in nitric acid, than of nitration in nitromethane, to catalysis by sulphuric acid, and to anticatalysis by metallic nitrates, will be clear. Pure nitric acid already contains so large a concentration of nitronium ion that a considerable addition of sulphuric acid is required to double it, and thus to double nitration rate; and a considerable addition of nitrate is required to halve it, and thus to halve nitration rate. The equilibrium concentration of nitronium ion in nitromethane solutions containing nitric acid is much smaller, and therefore proportionately considerable changes can be effected by means of much smaller additions of sulphuric acid or of nitrates. It can be estimated that the equilibrium concentration of nitronium ion in, for instance, 8·5M-nitric aid in nitromethane is of the order of 0·001M.

The reason why, in the various concentrations of nitric acid that have been used for nitrations in nitromethane, and also in nitric acid itself, the concentration of sulphuric acid required to double the rate is always of the same order of magnitude as the concentration of ionised nitrate needed to halve the rate will also be clear. It is simply that, in all conditions, apart from aqueous conditions which are the subject of another paper (Part III), comparable concentrations of nitronium ion and of nitrate ion are produced by the self-ionisation of nitric acid.

Comment may be made on the kinetic effect of water on first-order nitrations in nitric acid. The experimental result that the sensitivity of first-order nitrations towards anticatalysis by water is of the same order of magnitude as their sensitivity to anticatalysis by nitrates is in obvious agreement with the form of equation (19). However, there are several factors which

render consideration of the water effect quantitatively more complicated than that of the effect of nitrates.

For, first, except at quite low water concentrations, equilibrium (20) will probably have some importance, along with equilibrium (19), in fixing the stationary concentration of nitronium ion. Secondly, the concentration of nitrate ion is not only not buffered as the water concentration is varied: it will inevitably change with the water content, and will do so in a rather complicated way; for, on the one hand, water will destroy nitrate ion by equilibrium (19), and, on the other, it will produce nitrate ion by equilibrium (21); and thus, as water is progressively added, the concentration of nitrate ion must pass through a minimum—as, indeed, the electrical conductivity is known to do at a concentration about 2·2M. of water (Veley and Manley, *Proc. Roy. Soc.*, 1898, *A*, **191**, 365; Reed, unpublished work). The third source of complication is that much of what we call water is present in a bound form, as nitric acid hydrate.

$$HNO_3 + H_2O \rightleftharpoons NO_3^- + H_3O^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

It is difficult to assess the importance of the third of these effects, but on account of the first two we would expect the reciprocal of the first-order rate constant to increase with the water concentration according to a continually steepening curve. This is what is found, as Fig. 13 shows. It is probably significant that the steepening becomes sharp suddenly at water concentrations around 2·2M.; for this is the concentration which corresponds to the electrical conductivity minimum, and presumably corresponds approximately to the water concentration beyond which the content of nitrate ions begins to increase.

(Discussion continued on p. 2426.)

(3) Medium Effects on Nitration Kinetics: Mode of Action of the Nitronium Ion.

(3.0) *Significance of the Study of Solvent Effects.*—The observations to which attention will now be directed relate to solvent effects on rates of nitrations of different kinetic order, and on the kinetic order itself. The study of this subject is one of the ways in which we may discover the details of the last stage of the nitration process, *viz.*, the attack by the nitronium ion on the aromatic molecule.

The basis of the method is contained in the general theory of solvent effects on reaction rate (Hughes and Ingold, *J.*, 1935, 244; *idem et al.*, *J.*, 1948, 2043). A knowledge of the effect of solvent polarity, or ion-solvating power, on rate will tell us at once whether ions are formed or destroyed in the rate-controlling stage: polar solvents strongly accelerate reactions which generate ions and strongly retard those which consume ions. These are gross effects: if they are absent, a considerably weaker effect may sometimes be observed. It arises when an initially localised ionic charge becomes spread by mesomerism in the transition state of reaction; and it takes the form of a small retardation by polar solvents (for some illustrations, see Table III in the second of the papers cited above).

In the example of nitration, we can, by changing the reaction order, make rate-determining either the formation of the nitronium ion or its attack on the aromatic molecule. Hence, by studying solvent effects on nitrations of different orders, we can obtain the information indicated for each of the above stages, in particular, for the latter stage, which is now our main interest.

Our experiments on this part of the subject relate to the solvents acetic acid and nitromethane. But we shall be able to extend the conclusions thus derived to cover in a consistent way all that is known of medium effects on nitration in nitric acid and in sulphuric acid.

(3.1) *Observations on Medium Effects.*

(3.1.1) *Effect of Nitric Acid Concentration on Nitration Rate in Organic Solvents.*—Alike in Benford and Ingold's experiments on nitration in nitromethane, and in those now reported on nitration in this solvent and in acetic acid, the nitric acid has always been employed in a concentration sufficient to render it an important constituent of the solvent.

For nitration in nitromethane, Benford and Ingold found that the zeroth-order rate constants of benzene and more reactive aromatic hydrocarbons increased as the fifth or sixth power of the nitric acid concentration over the range of their observations. For the mixed-order reactions of the halogenobenzenes, no rate constants could be extracted from the kinetic observations, but the curvilinear rates themselves increased notably with the acid concentration. For the same solvent, nitromethane, we now find that the first-order rate constants of nitration

of *p*-dichlorobenzene, and other substituted benzenes of considerably reduced reactivity, also increase steeply with the concentration of nitric acid. Furthermore, we find all these effects repeating themselves in nitrations with acetic acid as the solvent. Some comparisons showing the effect of nitric acid concentration on zeroth-order and first-order rates in nitromethane, and in acetic acid, are given in Table XV. The experiments of each pair are so selected that the kinetic effect of nitrous acid, when not entirely negligible, is at least closely similar in the cases compared.

TABLE XV.

Effect of concentration of nitric acid on rate constants for nitration in organic solvents.

(Zeroth-order constants, k_0, in sec.$^{-1}$ g.-mol. l.$^{-1}$; first order constants, k_1, in sec.$^{-1}$.)

Expt.*	Order.	HAr.	Temp.	$[HNO_3]$.	$[HNO_2]$.	10^4k_0.	10^4k_1.
Solvent: Nitromethane:							
I 188	Zeroth	C_6H_6	0·0°	5·0	0·0089	3·28	—
I 294				7·0	0·0083	18·4	—
150	First	*p*-$C_6H_4Cl_2$	20·0	8·5	0·0240	—	367
156				11·5	0·0269	—	2470
Solvent: 99·8% Acetic acid:							
48	Zeroth	*p*-$C_6H_4Me_2$	20·0	5·0	0·0096	0·433	—
62				7·0	0·0046	6·17	—
281	First	*p*-$C_6H_4Cl_2$	20·0	10·5	0·0029	—	20·0
310				12·2	0·0034	—	223

* The numeral I distinguishes the experiments of Benford and Ingold's series (Part I, *loc. cit.*, from those of the present series.

(3.1.2) *Effect of Organic Solvents on Nitration Rate at a Constant Nitric Acid Concentration.*—Nitromethane is usually considered to be a more polar solvent than acetic acid. Nitromethane certainly has the larger dielectric constant and dipole moment. It is the better solvent for salts containing small ions. It is much the faster solvent for definitely ion-producing reactions, such as the formation of quaternary ammonium salts, and of sulphonium salts, from tertiary amines or alkyl sulphides and alkyl halides, sulphates, picrates, etc. Nitromethane is a much faster solvent than acetic acid for both zeroth-order and first-order nitration. This may be established by comparisons, with a fixed concentration of nitric acid, of rate constants for the nitration of any aromatic compound which reacts according to a common kinetic law in both solvents. Some examples are given in Table XVI.

TABLE XVI.

Effect of solvent polarity on rate constants for nitrations, with a fixed concentration of nitric acid, at 20·0°.

(Zeroth-order constants, k_0, in sec.$^{-1}$ g.-mol. l.$^{-1}$; first-order constants, k_1, in sec.$^{-1}$.)

Expt.	Order.	HAr.	$[HNO_3]$.	Solv.	$[HNO_3]$.	10^4k_0.	10^4k_1.
202 *	Zeroth	C_6H_5Me	7·0	$MeNO_2$	0·0046	188	—
60				AcOH	0·0050	5·90	—
156 †	First	*p*-$C_6H_4Cl_2$	11·5	$MeNO_2$	0·0030	—	3500
281, 164 ‡				AcOH	0·0030	—	81

* From the observed rate constant, $k_0 = 9·78 \times 10^{-4}$ sec.$^{-1}$ g.-mol. l.$^{-1}$ at − 10·0°, the quoted rate constant for 20·0° has been calculated by using Benford and Ingold's temperature coefficient (Part I, *loc. cit.*).

† From the observed rate constant, $k_1 = 2470 \times 10^{-4}$ sec.$^{-1}$ with $[HNO_3] = 0·0269$M., the quoted rate constant has been calculated to correspond with the lower nitrous acid concentration, 0·0030M., required for the comparison. The equation employed is $k_0^{-1} = a + b[HNO_2]^{3/2}$ with $b/a = 10$ (Benford and Ingold, Part I, *loc. cit.*).

‡ The quoted rate constant has been logarithmically interpolated between observed rate constants, $k_1 = 20·0 \times 10^{-4}$ sec.$^{-1}$ with $[HNO_3] = 10·5$M., and $k_1 = 165 \times 10^{-4}$ sec.$^{-1}$ with $[HNO_3] = 12·0$M., in order that it shall correspond to the nitric acid concentration, 11·5M., required for the comparison. The use of a power formula, instead of an exponential expression, gives practically the same result.

(3.1.3) *Effect of Nitric Acid Concentration on the Order of Reaction in an Organic Solvent.*—In certain cases it is possible to change the kinetic order of nitration in a given solvent by simply changing the concentration of nitric acid. The nitration of benzene in acetic acid provides an example. In 12·4M-nitric acid in this solvent, the nitration of benzene is very nearly of zeroth order; but in 7·0M-nitric acid in the same solvent the reaction is very nearly of first order. How

closely these approximations hold can be shown by means of the comparisons, set out in Table XVII, of the rate constants for nitration of benzene and toluene under identical conditions.

TABLE XVII.

Effect of nitric acid concentration on the kinetic order of nitration of benzene in 99·8% acetic acid.

(Zeroth-order constants, k_0, in sec.$^{-1}$ g.-mol. l.$^{-1}$; first-order constant, k_1, in sec.$^{-1}$.)

Expt.	HAr.	$[HNO_3]$.	Temp.	$[HNO_3]$.	$[HAr]_0$.	10^5k_0.	10^2k_1.
79	C_6H_6	12·4	10·7°	0·497	0·353	97	—
80	C_6H_5Me			0·497	0·352	103	—
78	C_6H_6	7·0	20·0	0·0051	0·100	—	4·02
60	C_6H_5Me			0·0050	0·100	5·90	—

Toluene nitrates according to a zeroth-order kinetic law under the conditions of both the comparisons. If in either case the nitration of benzene followed a zeroth-order law exactly, it should in that case have identically the same rate-constant. Furthermore, the nitration of benzene could only follow a first-order law exactly if its absolute rate (not rate-constant) were indefinitely small in comparison with the zeroth-order rate of nitration of toluene.

From the figures given it appears that, in 12·4M-nitric acid, the zeroth-order rate of nitration of benzene is smaller by 6% than the zeroth-order rate of nitration of toluene under the same conditions. In competition experiments benzene is nitrated about 24 times more slowly than toluene. We conclude that the slightly smaller kinetic rate for benzene means that its nitration rate is not quite rigidly fixed by the rate of formation of the nitronium ion, but is being slightly restricted by the relatively low reactivity of the benzene molecule itself. Again, from figures given it appears also that, in 7·0M-nitric acid, the initial rate of nitration of benzene in 0·1M-concentration is smaller than what would be the steady rate if the reaction had followed a zeroth-order law by the factor $(4·02/5·90) \times 0·1 = 1/15$. We know what this steady rate would be, because it would be the same as the actually observed steady rate for the nitration of toluene in the same conditions. Thus the nitration of benzene starts with only 7% of its zeroth-order velocity, and, as the reaction proceeds, it becomes continually slower, both absolutely and relatively. These factors, 0·07 falling to zero, by which the actual reaction is slower than the zeroth-order reaction, measure the extent to which the existence of zeroth-order aromatic nitration must cause a deviation from strict first-order kinetics in the nitration of benzene in these conditions. This consideration of the deviations from integral reaction-orders only serves to emphasize that the change of order, produced by the change of nitric acid concentration, is very nearly integral.

(3.1.4) *Effect of Organic Solvents on the Order of Reaction at a Common Nitric Acid Concentration.*—As compared with nitration in nitromethane, nitrations in acetic acid show a generally smaller tendency towards zeroth-order kinetics and a greater towards first-order kinetics. This statement assumes that one compares the effect of the two solvents on reaction order at a common concentration of nitric acid. In illustration, we shall refer again to the nitration of benzene.

Benford and Ingold studied the nitration of benzene in nitromethane, with nitric acid at various concentrations extending over the range 3·0—7·0M.; and over the whole of this range they observed zeroth-order kinetics (Part I, *loc. cit.*). We have studied the nitration of benzene in acetic acid, with nitric acid in a series of concentrations extending over the range 7·0—12·4M.; and over this range, as we have just seen, the reaction order drops from first to zeroth.

TABLE XVIII.

Effect of solvent polarity on the kinetic order of the nitration of benzene with 7·0M-nitric acid.

(Rate constants: k_0 in sec.$^{-1}$ g.-mol. l.$^{-1}$, and k_1 in sec.$^{-1}$.)

Expt.	Solvent.	Order.	Temp.	$[HNO_3]$.	$[HAr]_0$.	10^5k_0.	10^2k_1.
294—299 *	$MeNO_2$	Zeroth	0·0°	0·0051	0·10	17·2	—
78	AcOH	First	20·0	0·0051	0·10	—	4·02

* Expts. nos. 294—299 of Part I (*loc. cit.*) covered the range of concentration of nitrous acid 0·0083M. to 0·1500M., and gave the rate formula $k_0^{-1} = 10^4(0·35 + 3·30[HNO_2]^{1/2})$. From this the quoted rate constant is calculated to correspond to the concentration of nitrous acid, 0·0051M., required for the comparison.

A comparison of the kinetic effects of the two solvents, nitric acid being at the common concentration 7·0M., is shown in Table XVIII. It appears that the effect on the reaction order of replacing acetic acid by nitromethane, with this fixed concentration of nitric acid, is much

like that of retaining acetic acid as the solvent, but substantially increasing the proportion of nitric acid dissolved in it. Each change presumably increases the polarity of the medium; and each change in fact produces a unit drop in the kinetic order of nitration.

(3.2) *Discussion* (*Part* 3): *Medium Effects*: *Mode of Action of the Nitronium Ion*
(continued from p. 2423).

(3.2.1) *Molecularity of Aromatic Attack by the Nitronium Ion in Organic Solvents.*—In Part 1 of this Discussion we established the formation and effectiveness of the nitronium ion in nitration, essentially by means of a study of the variations in the kinetic order of reaction. We then set down (p. 2411) schemes (11) and (12), as representing in detail the reactions which produce the nitronium ion, in the presence, and in the absence, of acids stronger than nitric acid. We also set down (p. 2412) equations (13) and (14), expressing two alternative methods by which the nitronium ion might attack and nitrate an aromatic molecule. In Part 2 of the Discussion we were concerned to elucidate the reaction stages involved in the formation of the nitronium ion. Evidence on the matter was derived from a study of the kinetic effects of certain solutes. We thus established the correctness of schemes (11) and (12), which make the nitric acidium ion an essential precursor of the nitronium ion. Continuing our Discussion, we shall now attempt a decision between the alternative modes of action of the nitronium ion, as represented by equations (13) and (14), our evidence being derived from the study of medium effects on reaction rate and reaction order.

Equation (13) represents what we call the "bimolecular" mechanism of nitronium ion attack. It implies that, very quickly after the nitronium ion becomes attached to the aromatic carbon atom, the aromatic proton is ejected into the solvent, without waiting to be extracted by a solute base, such as hydrogen sulphate or nitrate ion. In this case the proton transfer is too rapid to be kinetically significant, and the reaction is not base-accelerated.

Equation (14) expresses what we term the "termolecular" mechanism of nitronium ion attack. Here the picture is that, after the uptake of the nitronium ion, the proton remains in aromatic combination until it is found, and extracted, by a sufficiently powerful base. In this event the proton transfer is an important part of the rate-determining reaction-stage, and the reaction will be base-accelerated.

We shall first consider the effects to be expected from this distinction of mechanism in relation to the evidence concerning nitration in the absence of acids stronger than nitric acid. Accordingly we shall take equation (12) as expressing in detail the formation of the nitronium ion. Equations (13) and (14) are alternative representations of the mode of action of the nitronium ion.

It will simplify reference to the processes involved if we first express the combination of equation (12) with either equation (13) or equation (14) in the summarised form (22):

$$HNO_3 \underset{(b)}{\overset{(a)}{\rightleftharpoons}} NO_2^+ \xrightarrow[(c)]{} NO_2Ar \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

This is done for the convenience of being able to use the labels (*a*), (*b*), and (*c*) for groups of associated reaction-stages. Process (*a*) signifies all the forward transformations involved in the conversion of a nitric acid molecule into a nitronium ion. Process (*b*) denotes the reversal of this group of transformations. Process (*c*) represents the final phase of nitration by the nitronium ion, *i.e.*, its actual attack on the aromatic molecule, together with the associated proton-transfer. We take equations (12) as the expressions of processes (*a*) and (*b*) together. At first we shall assume equation (13) to express process (*c*).

As can be seen from equations (12), process (*a*) converts three neutral molecules into one neutral molecule and two ions. This process will be much accelerated by the increased solvation forces of a more polar medium. For corresponding reasons the reverse process, (*b*), should be strongly retarded by an increase in the polarity of the medium. Process (*c*), as expressed by equation (13), neither creates nor destroys ionic charges in its rate-determining stage. In the first approximation in which we shall consider the gross kinetic effects, the rate of this reaction should be unaffected by the polarity of the medium.

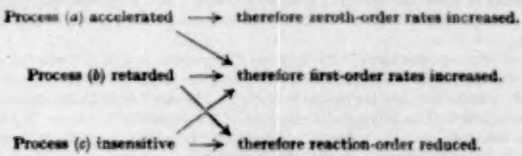
Putting these points together, we shall find that we can satisfactorily interpret all the main kinetic effects of solvent changes on the basis of the hypothesis that the bimolecular equation (13) really does express process (*c*). The argument is as follows.

The measured zeroth-order rates depend only on process (*a*). These zeroth-order reactions will therefore be strongly accelerated by increases in the polarity of the medium, such as might be produced by increase of nitric acid content, or a replacement of acetic acid by nitromethane.

The measured first-order rates are constituted as products of two factors. One factor is the stationary concentration of nitronium ion. This will closely approximate to an equilibrium concentration determined by the reversible conversion of three neutral molecules into one molecule and two ions. It follows that the stationary concentration of nitronium ion will be strongly increased by an increase in the polarity of the medium. The second factor is the specific rate of process (*c*). But, as we have already seen, this should, in our first approximation, be insensitive to changes in the medium. It follows that the complete first-order reactions must be strongly accelerated by increases in the polarity of the medium.

The kinetic order of nitration depends on what fate principally befalls the nitronium ion, and, in particular, on whether what is formed by process (*a*) is mostly destroyed by process (*b*) or by process (*c*). The former alternative leads to first-order kinetics, and the latter to zero-order kinetics; and thus the observed reaction order will depend on the ratio of the rates of processes (*b*) and (*c*). Since process (*b*) must be retarded by an increase in the polarity of the medium, whereas, in our present approximation, process (*c*) is insensitive to changes in the medium, it follows that the effect of a change to a more polar medium must be in the direction of replacing process (*b*) by process (*c*); that is, it must be in the direction of reducing the order of the over-all reaction from first order towards zeroth order.

We may assemble these deductions in the following summary of expected effects of increasing the polarity of the medium:



All these deductions have been experimentally verified.

The success of these deductions is definitely dependent on the choice of the "bimolecular" equation (13), rather than the "termolecular" equation (14), as representing process (*c*). Suppose that we allow equations (12) to represent processes (*a*) and (*b*) as before, but now assume that equation (14) expresses process (*c*). Then, since, according to equation (14), two ions disappear, becoming replaced by neutral molecules (cf. p. 2412), process (*c*) must be strongly retarded by an increase in the polarity of the medium. Indeed, process (*c*) should be retarded comparably to process (*b*); and hence we should not expect that first-order rates should be increased at least as sharply as zeroth-order rates, as media are made more polar; and we should not expect that reaction orders would be reduced in such circumstances. Thus our observations on medium effects provide a strong support for the bimolecular picture of nitronium ion attack, as expressed in equation (13).

(3.2.2) *Molecularity of Aromatic Attack by the Nitronium Ion in Nitric Acid.*—For the nitration of benzene in acetic acid, the reaction order is changed from first to zeroth when we replace a part of the acetic acid by nitric acid, as we do by increasing the nitric acid concentration from 7·0M. to 12·4M. According to our interpretation of medium effects, we should certainly expect the order of nitration of benzene to remain zeroth when we replace the rest of the acetic acid by nitric acid. However, all the kinetically observed nitrations in nitric acid are first-order reactions.

The reason for this is obviously to be sought in the changes that one has had to make in the nature of the aromatic compound in order to secure nitration rates low enough for measurement in pure nitric acid. A direct kinetic observation of the mononitration of benzene in nitric acid is scarcely possible, because of the very high speed of nitration of benzene in this medium. In order to obtain a measurable reaction rate, one has to introduce some strongly deactivating group, such as a nitro-group. It would not be unreasonable to estimate that a nitro-substituent reduces the specific rate of a nitrating attack on the benzene molecule by a factor of the order of 10^{-6}. Kharasch and Westheimer have suggested the more extreme value 10^{-7}. The precise value, however, is immaterial, for it is in any case intelligible that, when a constitutional change reduces the specific rate of process (*c*) by any factor such as either of these, process (*b*) will recover its position as the main mode of destruction of the nitronium ion, and we shall again observe a reaction of the first order.

These high speeds of nitration in pure nitric acid point to the conclusion that in this solvent,

as in organic solvents, the attack of the nitronium ion on the aromatic molecule follows the bimolecular mechanism represented in equation (13), and not the termolecular mechanism of equation (14). In order to illustrate the argument, let us take 10^{-4} as the factor by which a nitro-group reduces the rate of a nitrating attack on an aromatic molecule. We know that benzene may be nitrated at a measurable first-order rate by 7M-nitric acid in acetic acid, and that nitrobenzene may be nitrated at a measurable first-order rate by pure nitric acid. Employing our illustrative factor, we may assume that nitrobenzene is nitrated about 10^4 times faster in pure nitric acid than it would be by 7M-nitric acid in acetic acid. Again the exact ratio is immaterial; for clearly it would be impossible to understand an increase of rate by any such large factor on passing over from solvent acetic acid to solvent nitric acid, if any one of the stages of the forward reaction were required by theory to become continually and very markedly *slower* as the polarity of the medium is continually increased. And this is what the "termolecular" theory of nitronium ion attack does require of process (*c*). Accordingly, it seems that, by this simple argument, we may exclude the termolecular theory, with its implications that the reaction is base-accelerated, and that the extraction of the aromatic proton is kinetically important. The bimolecular theory, in its first approximation, requires that the specific rate of process (*c*) will not be greatly affected by the solvent, so that first-order nitration rates will follow, more or less closely, the stationary concentration of nitronium ion, which will increase strongly and continually as the medium increases in polarity. This inference is consistent with the general kinetic picture. We conclude that the nitronium ion attacks by the bimolecular mechanism, and that the aromatic proton is lost in a subsequent, fast reaction-stage.

(3.2.3) *Molecularity of Aromatic Attack by the Nitronium Ion in Sulphuric Acid.*—We shall continue to use the labels of scheme (22) in our discussion of the stages involved in nitration in sulphuric acid. But now, since sulphuric acid is a stronger acid than nitric acid, we have to regard processes (*a*) and (*b*) as interpreted in detail by equations (11) on p. 2411. The question for discussion is whether, in this solvent, process (*c*), the attack of the nitronium ion on the aromatic molecule, is to be identified with the bimolecular process of equation (13), or with the termolecular process of equation (14). We shall again conclude that the attack of the nitronium ion is bimolecular, the aromatic proton being lost in a subsequent, fast reaction-stage.

The broadest argument in favour of this view is on the lines of that just given in relation to nitration in nitric acid. For sulphuric acid, even more than nitric acid, is a highly polar solvent. And in sulphuric acid rates of nitration are very great in comparison with the rates observed in moderately polar organic solvents. This would be unintelligible if the nitration process contained any essential forward step which theory required to be strongly and continuously *retarded* as the medium is made more and more polar. This simple consideration appears to exclude the termolecular theory of nitronium ion attack, as represented in equation (14). On the other hand, the bimolecular theory, expressed by equation (13), is, as before, fully consistent with the general kinetic picture. It is implied that, for nitration in sulphuric acid, the elimination of the aromatic proton has no kinetic importance.

The contrary view, that for nitration in sulphuric acid the loss of the aromatic proton is kinetically significant, has been advocated by Bennett, Brand, James, Saunders, and Williams (*loc. cit.*), who first used a termolecular equation of the type of equation (14). Their object was to explain the fact, discovered by Martinsen (*loc. cit.*), and confirmed by many investigators since, that the addition of a few units per cent. of water to sulphuric acid increases nitration rate in that solvent (although the addition of much more water strongly decreases the rate). The explanation assumes a mass-law acceleration by hydrogen sulphate ions, acting as the base B^- of equation (14). In our view, this theory* envisages too small a range of observations, and neglects the general kinetic situation outlined above.

An effect of the type of that discovered by Martinsen should be expected on the basis of the bimolecular theory of process (*c*), as expressed in equation (13). For simplicity, let us suppose that, by keeping the added nitric acid in constant excess over the aromatic compound, we cause

* Some significance appears to have been attached to the expression of this theory in an algebraic equation by means of which the variation of nitration rate with the water content of the sulphuric acid can approximately be reproduced. We think, however, that the degree of agreement exhibited is largely a mathematical necessity, arising in part from the circumstance that the rate must follow the nitronium ion concentration when the latter is varying strongly, as it is in the more aqueous end of the solvent range, and in part from the method of choosing the disposable constants, which automatically secures a tolerable fit in the less aqueous end of the range, where the concentration of nitronium ion must always be close to its stoicheiometric limit. A recent defence of the theory by Bennett (*Chem. and Ind.*, 1949, 235) lacks appreciation of this point.

the usual second-order nitration rates observed in sulphuric acid to degenerate into first-order rates, so that we can consider them collectively and continuously with the previously discussed first-order rates in less polar media, such as nitric acid, nitromethane, and acetic acid. We noted [Section (3.2.1)] that these first-order rates can be regarded as composed from products of a stationary concentration of nitronium ion and a specific rate of aromatic attack by the nitronium ion; and that, in the formation of the nitronium ion, ionic charges are created, whilst, in the aromatic attack of the nitronium ion, a previously concentrated ionic charge becomes spread into the aromatic ring. By using the solvent theory in its crudest form, which takes account only of the formation and destruction of charges, but not of their degree of distribution, we related the gross rate changes which accompany an increase of solvent polarity, from that of acetic acid in the direction of that of sulphuric acid, essentially to increases in the stationary concentration of nitronium ion, neglecting in comparison the changes in the specific rate of its attack upon the aromatic ring. Such neglect, however, will no longer be admissible when the stationary concentration of nitronium ion has increased to near its stoicheiometric limit. And this happens in solvent sulphuric acid containing less than about 7% (or 30 mols. %) of water. The concentration of nitronium ion, now determined by its substantially quantitative formation, is buffered against further medium change; and therefore we have now to look more carefully at the second factor which enters into the determination of first-order nitration rates, *viz.*, the specific rate of attack by the nitronium ion on the aromatic nucleus. For this purpose, we must use the solvent theory in its second approximation which takes account of the degree of distribution of ionic charges.

Sulphuric acid is a highly polar solvent: its dielectric properties are much more extreme than are those of water (Gillespie, Hughes, and Ingold, *J.*, 1950, paper no. **497**). Partly because, contrary to previously held opinion, water is not fully ionised in sulphuric acid (Gillespie, *J.*, 1950, paper no. **498**), and partly because it is considerably ionised (the ionisation causing Debye "cavities" to occupy much of the medium), it seems certain that the first effect of adding water to sulphuric acid will be to reduce solvating power.

According to the bimolecular theory of aromatic attack by the nitronium ion, as expressed in equation (13), there is a spreading of charge in the formation of the transition state. Therefore the effect of a reduction of the solvating power of the solvent will be to increase the rate of the attack. Knowing the orders of magnitude of solvent effects due to charge distribution in other cases, it seems reasonable to assume that this particular charge-spreading would cause the rate of aromatic attack to increase by some quite small multiple (such as 2 or 4) as solvating power is reduced by adding water up to 30 mols. % to the solvent sulphuric acid. If it were not for a disturbance which is mentioned below, such a rate increase would appear with but slight modification in the observed nitration rates, because of the nearly stoicheiometric formation of nitronium ion. (Of course, the addition of much more water will reduce nitration rate by reversing the reactions of equations (11), by which the nitronium ion is formed.)

Even if we could put this theory into a quantitative form, we should not expect it to agree with the published data for the dependence of nitration rate on the water content of solvent sulphuric acid; for, as Gillespie and Millen have pointed out (*Quart. Reviews*, 1948, **2**, 277; cf. Baddely, Graddon, and Kenner, *Nature*, 1947, **160**, 187), a complication enters in nearly all real cases. It is that most substances, whose nitration rates in sulphuric acid have been studied, combine with the acid to form unreactive salt-like complexes, which added water will partly break up, thereby facilitating nitration. This effect on rate is of the same qualitative form as the solvent effect deduced above, and therefore the observed result is in general a combination of both effects. In many cases, *e.g.*, for nitro-compounds, complex formation probably contributes appreciably to the total result, whilst in some examples, *e.g.*, benzoic acid, it probably plays a major rôle These differences arise from differences in the basicity of the aromatic compounds (Gillespie, *J.*, 1950, paper no. **503**); and they doubtless explain why the sensitivity of nitration rate in sulphuric acid to water content varies as much as it does from case to case.

Our conclusion is, then, that neither in solvent sulphuric acid, nor in any of the other solvents considered in this paper, has the loss of the aromatic proton any concern with the rate-determining stage of nitration. There is a simple way of confirming or disproving this proposition, by using the principle of the differing zero-point energies of the hydrogen isotopes. If the proton loss has no kinetic importance, as the bimolecular mechanism of equation (13) assumes, then identically situated aromatic protium and deuterium should be displaced by an entering nitro-group at identical rates; whereas if the proton loss is kinetically significant, as the termolecular mechanism of equation (14) demands, then we must expect protium to be displaced from 3 to more than 10 times faster than deuterium. We were engaged (jointly with Drs. Gillespie and

Millen) in trying these experiments, when we heard from Dr. L. Melander that he had completed some similar experiments, using tritium instead of deuterium as the heavier hydrogen isotope. His uniform result is that the rates of displacement of the isotopes are accurately identical.*

On all these grounds it seems clear that the attack of the nitronium ion on the aromatic molecule in the solvents we have considered is a two-stage bimolecular process, a slow uptake of the nitronium ion being succeeded by a rapid loss of the aromatic proton, in accordance with equation (13) on p. 2412. The establishment of this conclusion completes the central part of our kinetic analysis of the process of aromatic nitration by nitronium ions derived from nitric acid.

(Discussion continued on p. 2434.)

(4) Effect of Nitrous Acid on Nitration Kinetics: Condition of Nitrous Acid in Nitric Acid Solvents.

(4.0) *Significance of the Kinetic Effects of Nitrous Acid.*—Here, as elsewhere in this paper, the term "nitrous acid" is used to include all those materials, present in nitric acid media, which in the water-diluted solution are together analytically determined as nitrous acid.

The original observation on the kinetic influence of nitrous acid was that of Benford and Ingold (Part I), who noted that the presence of this material caused a marked reduction in the rates of zeroth-order nitrations in nitromethane. There are two general causes of homogeneous anticatalysis, *viz.*, the breaking of reaction chains, and the retrogression of reversible reaction stages. Benford and Ingold adopted the former hypothesis as providing the more plausible explanation of their effect; for they could suppose that the nitrous acid was supplying nitrogen dioxide, or some other free-radical chain-breaker. Thus they were led to the inference that nitration under their conditions was a chain reaction. Our much wider kinetic investigation has, however, shown that nitration is not a chain reaction. Accordingly, the interpretation of the anticatalytic effect of nitrous acid needs reconsideration.

The solution of this problem is quite simple. In the course of our investigation of the kinetics of nitration, we encountered an anticatalytic effect which is more powerful than that of nitrous acid, *viz.*, the effect of nitrate ions; and we showed that this effect works by reversing a reaction stage. It will be established that nitrous acid, when present in nitric acid media, produces nitrate ions; and that it is these which are responsible for the observed anticatalytic effect of nitrous acid.

It follows from this interpretation that the kinetic study of the effect of nitrous acid on nitration provides a means of obtaining information about the molecular condition of nitrous acid in solvent nitric acid, *i.e.*, about the ionic and molecular species present in "yellow nitric acid." Complementary information has been yielded by the study of the physical properties of yellow nitric acid, notably of its spectroscopic and electrolytic properties, of which the former are described in an accompanying paper by Goulden and Millen (*J.*, 1950, paper no. 511), while the latter will be reported shortly. But before taking the physical evidence into account, we have to record some new extensions of the experimental study of the kinetic effects of nitrous acid on nitration.

(4.1) *Observations on the Kinetic Effects of Nitrous Acid.*

(4.1.1) *Constancy of the Concentrations of Nitrous Acid.*—Benford and Ingold commenced their study of the effect of nitrous acid on zeroth-order nitrations in nitromethane by showing that, under these conditions of nitration, nitrous acid is a true negative catalyst, *i.e.*, that, whilst affecting the rate of nitration, it is not itself either formed or destroyed in the nitration process. When extending the study of the effect of nitrous acid to first-order nitrations in nitromethane, and to zeroth- and first-order nitrations in other media, it was necessary to ascertain, for these cases also, whether the concentration of nitrous acid in a nitration solution does, or does not, remain undisturbed by the occurrence of nitration.

This was ascertained by determining the nitrous acid before and after nitration. The uniform result, obtained in a representative series of cases covering all the nitration media, types of aromatic compound, and kinetic forms of nitration, considered in this paper, was that the concentration of nitrous acid before and after nitration agreed to within the error of the analytical determination. A sample of such results is contained in Table XIX.

* Since this was written the work cited has been published in summary (Melander, *Nature*, 1949, **163**, 599; *Acta Chem. Scand.*, 1949, **3**, 95). Its agreement with our kinetic data has also been briefly pointed out (Gillespie, Hughes, Ingold, Millen, and Reed, *Nature*, 1949, **163**, 599). [*Added in proof.*] A full account has just appeared (*Arkiv Kemi*, 1950, **2**, 211).

Exceptions to the rule that nitrous acid is neither formed nor destroyed have been encountered in the nitration of certain (but by no means all) derivatives of phenol and aniline. Such nitrations display a somewhat complicated kinetic form, with nitrous acid functioning as a positive catalyst in certain conditions. These nitrations are not our present concern, since they involve special mechanisms. They are discussed in the accompanying papers, Parts VI and VII; *J.*, 1950, papers nos. 512, 513).

TABLE XIX.

Illustrating the constancy of the concentrations of nitrous acid during nitrations at 20·0°.

Expt.	Solvent.	HAr.	$[HNO_2]_0$.	$[HNO_2]_{initial}$.	$[HNO_2]_{final}$.
15	$MeNO_2$	*p*-$C_6H_4Cl_2$	8·5	0·00164	0·00170
16	,,	,,	,,	0·00172	0·00174
18	AcOH	C_6H_5Me	6·0	0·00049	0·00049
11	,,	C_6H_6	9·5	0·493	0·505
12	,,	,,	—	0·503	0·500

(4.1.2) *Effect of Nitrous Acid on Nitrations in Nitromethane.*—The case of zeroth-order nitrations in this solvent was dealt with comprehensively by Benford and Ingold (Part I). They showed, in the examples of benzene and its homologues, that the rate of nitration was decreased by nitrous acid in such a way that the reciprocal of the rate increased linearly with the square-root of the concentration of nitrous acid. The formula $1/k_0 = a_0 + b_0[HNO_2]^{1/2}$ held over the whole of the investigated range of conditions, *viz.*, for nitric acid concentrations between 3M. and 7M., and for nitrous acid concentrations up to about 0·1M. or rather more. All the observed retardations took place without sensible disturbance to the zeroth-order form of the reactions.

Some experiments have been carried out which extend the range of Benford and Ingold's observations to higher concentrations of nitrous acid. Here a disturbance is experienced: at concentrations well above 0·1M., the anticatalytic effect increases with concentration considerably more steeply than corresponds to the equation written above. This is established by the rate constants quoted in Table XX. However, even the most strongly retarded reactions showed no detectable departure from the zeroth-order kinetic form.

TABLE XX.

Effect of nitrous acid on zeroth-order rate constants (k_0 *in sec.*$^{-1}$*g.-mol.l.*$^{-1}$) *for the nitration of toluene in nitromethane* (cf. Part I, Table II).

$[HNO_3] = 7·0$M. $[HAr]_0 = 0·09$M. Temp. $= -6·0°$.

Expt.	$[HNO_2]_0$.	10^4k_0.	Expt.	$[HNO_2]_0$.	10^4k_0.	Expt.	$[HNO_2]_0$.	10^4k_0.
611	0·0038	7·78	617	0·0755	3·45	615	0·420	0·70
612	0·0253	4·93	614	0·170	1·84	616	0·448	0·64

This incursion of a specially strong anticatalysis at high nitrous acid concentrations appears to be a general phenomenon. It is illustrated for the zeroth-order nitrations in nitromethane in Fig. 14, where it appears as a deviation from a straight line representing the anticatalytic law established by Benford and Ingold for low concentrations of nitrous acid. The continuous line represents the approximate range of validity of their law.

Benford and Ingold showed (*loc. cit.*) that the mixed-order nitrations, which the four monohalogenobenzenes undergo in nitromethane, are also subject to anticatalysis by nitrous acid.

We now find that first-order nitrations in nitromethane are subject to a closely similar anticatalysis by nitrous acid. Some first-order rate constants for the nitration of *p*-dichlorobenzene in the presence of various amounts of nitrous acid are assembled in Table XXI. Even the strongest retardations are unaccompanied by any discernible disturbance to the first-order kinetic form of nitration.

TABLE XXI.

Effect of nitrous acid on first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of p-dichlorobenzene in nitromethane.*

$[HNO_3] = 8·8$M. $[HAr]_0 = 0·10$M. Temp. $= 20·0°$.

Expt.	$[HNO_2]_0$.	10^4k_1.	Expt.	$[HNO_2]_0$.	10^4k_1.	Expt.	$[HNO_2]_0$.	10^4k_1.	Expt.	$[HNO_2]_0$.	10^4k_1.
301	0·0018	649	622	0·0250	276	623	0·0590	218	154	0·0829	187
150	0·0240	367	152	0·0365	298	153	0·0805	215	626	0·106	100
21	0·0240	360	151	0·0480	255	624	0·0676	194	628	0·174	45

If we temporarily leave aside the last two experiments, and plot the reciprocals of the rate constants against the square-roots of the nitrous acid concentrations, we obtain the linear relation shown in Fig. 15. Thus it appears that, for concentrations of nitrous acid which are not too high, the law obeyed by the anticatalysis is $1/k_1 = a_1 + b_1[HNO_2]^{1/2}$; that is, it is of the same form as for zeroth-order nitration, except, of course, that the constants, k_1, a_1, and b_1, have not the same physical dimensions as the constants, k_0, a_0, and b_0, which apply to the zeroth-order case.

FIG. 14.

Effect of nitrous acid on the zeroth-order rate of nitration of toluene by 7·0M-nitric acid in nitromethane at 0·0°.

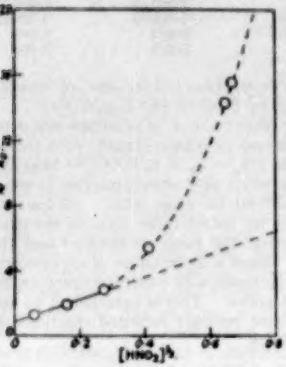
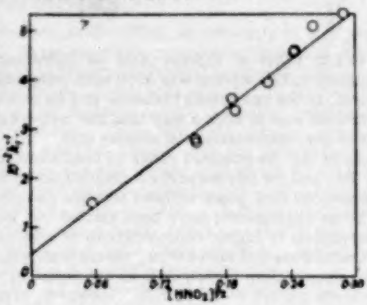


FIG. 15.

Effect of nitrous acid on the first-order rate of nitration of p-dichlorobenzene by 8·5M-nitric acid in nitromethane at 20·0°.



The last two experiments noted in Table XXI suffice to show, however, that this law is only a limiting law: the points representing these two experiments lie well above the projection of the straight line shown in Fig. 15. The complete graph is a straight line running into a rapidly steepening curve, much as in Fig. 14. We conclude that in first-order nitrations in nitromethane, just as in zeroth-order nitrations in this solvent, a specially powerful anticatalysis supervenes at the higher concentrations of nitrous acid.

(4.1.3) *Effect of Nitrous Acid on Nitrations in Acetic Acid.*—This has been investigated in the examples of the zeroth-order nitration of toluene in 7M- and in 12M-nitric acid, the zeroth-order nitration of benzene in 12M-nitric acid, the first-order nitration of benzene in 8M-nitric acid, and the first-order nitration of chlorobenzene in 10M-nitric acid. The kinetic phenomena observed in these cases are generally similar to those described in section (4.1.2).

In all cases nitrous acid reduces the reaction rate, without noticeably altering the kinetic form of the reaction: zeroth- and first-order reactions alike are retarded. The limiting form, for low concentrations of nitrous acid, of the law expressing the retardations appears to be the same for these nitrations in acetic acid as for nitrations in nitromethane, *viz.*, $k_0^{-1} = a_0 + b_0[HNO_2]^{1/2}$ for the zeroth-order reactions, and $k_1^{-1} = a_1 + b_1[HNO_2]^{1/2}$ for the first-order reactions. However, at concentrations of nitrous acid above about 0·1M., an anticatalytic effect supervenes which is much stronger than corresponds to the above limiting law. The results in Table XXII will serve to establish these points in the example of the nitration of chlorobenzene.

TABLE XXII.

Effect of nitrous acid on first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of chlorobenzene in 99·8% acetic acid.*

$[HNO_2] = 10·0$M. $[HAr]_0 = 0·10$M. Temp. = 20·0°.

Expt.	$[HNO_2]$.	10^4k_1.	Expt.	$[HNO_2]$.	10^4k_1.	Expt.	$[HNO_2]$.	10^4k_1.
291	0·0022	325	177	0·0450	182	174	0·146	43·8
170	0·0036	281	173	0·101	119	176	0·160	41·8
171	0·0128	241	175	0·135	81·4	178	0·203	15·0
172	0·0243	211						

A plot of the reciprocals of the rate-constants, given in Table XXII, against the square-roots of the nitrous acid concentration is shown in Fig. 16. From this graph it appears that the linear relationship representing the limiting law has approximate validity up to about 0·1M-nitrous acid, but that at higher concentrations than this the anticatalytic effect becomes intensified very rapidly.

(4.1.4) *Effect of Nitrous Acid on Nitrations in Nitric Acid.*—First-order nitrations with nitric acid as both solvent and reagent are also retarded by nitrous acid, the kinetic order of the reaction remaining undisturbed. This has been established in the examples of the nitration of nitrobenzene and of 1-nitroanthraquinone. Some data relating to the nitration of nitrobenzene in nitric acid containing nitrous acid are given in Table XXIII. It should be observed that, except for the nitrous acid (introduced as dinitrogen tetroxide), and the compound undergoing nitration, and its nitration products, the nitric acid used in these experiments was pure; for we

FIG. 16.

Effect of nitrous acid on first-order rate of nitration of chlorobenzene by 10·0M-nitric acid in acetic acid at 20·0°.

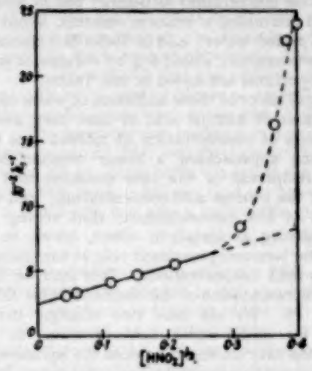
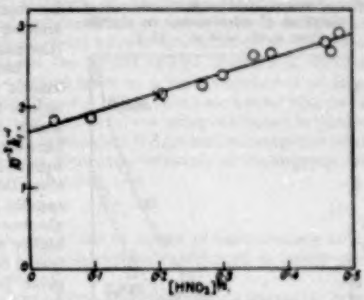


FIG. 17.

Effect of nitrous acid on first-order rate of nitration of nitrobenzene in anhydrous nitric acid at −13·3°.



(× = *Point derived from Fig.* 13.)

shall note below that the kinetic effect of nitrous acid is very different when the employed nitric acid contains water.

TABLE XXIII.

Effect of nitrous acid on first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of nitrobenzene in 100·0% nitric acid.*

$[HNO_3]_a$ = 24·58M.* $[H_2O]$ = 0·00M. $[HAr]_a$ = 0·20M. Temp. = −13·3°.

Expt.	$[HNO_2]_a$.	10^4k_1.	Expt.	$[HNO_2]_a$.	10^4k_1.	Expt.	$[HNO_2]_a$.	10^4k_1.
410	0·0015	547	417	0·0912	401	415	0·221	375
414	0·0094	536	419	0·121	378	421	0·211	357
416	0·0428	461	420	0·138	375	422	0·229	342
418	0·0734	426						

* Molarity before the introduction of nitrous acid or nitrobenzene (cf. p. 2418).

The retardations caused by nitrous acid in the speed of nitration are much smaller in pure nitric acid than they are in organic solvents: the largest of the nitrous acid concentrations used cut down the rate only by about one-third. Because of this, we are not able to establish the mathematical form of the effect with a chemically significant degree of precision. It is true that, as Fig. 17 shows, a plot of the reciprocals of the rate constants against the square-roots of the nitrous acid concentrations can be considered to indicate a straight line; but this is hardly significant because of the smallness of the effect. What Fig. 17 does show is that, up to nitrous acid concentrations of 0·23M., there are no signs of the incursion of a much more powerful anticatalysis of the type of that which, in organic solvents, supervenes at concentrations of nitrous acid above about 0·1M.

TABLE XXIV.

Effect of nitrous acid on first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of nitrobenzene in nitric acid containing water.

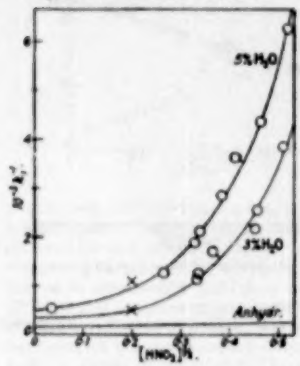
Expt.	$[HNO_2]_0$.	10^5k_1.	Expt.	$[HNO_2]_0$.	10^5k_1.	Expt.	$[HNO_2]_0$.	10^5k_1.
Series A: $[HNO_3]_0$ = 23·66M.*			$[H_2O]_0$ = 1·65M.†			$[HAr]_0$ = 0·21M.		Temp. = − 13·3°.
631	0·110	88·2	633	0·132	57·8	635	0·210	39·4
632	0·113	79·5	634	0·207	46·6	636	0·259	25·8
Series B: $[HNO_3]_0$ = 23·36M.*			$[H_2O]_0$ = 2·93M.†		$[HAr]_0$ = 0·20M.			Temp. = − 13·3°.
425	0·00135	189	427	0·116	47·2	432	0·220	22·8
426	0·0702	78·6	429	0·148	34·9	430	0·273	15·9
428	0·109	53·1	431	0·166	27·2			

* Molarity before introduction of nitrous acid or nitrobenzene (cf. p. 2418).
† These figures relate to initially added water: extra water is produced during the nitrations.

The influence of added water on the kinetic effect of nitrous acid is illustrated by the two series of results in Table XXIV. They again relate to the nitration of nitrobenzene in nitric acid, at the same temperature as before; but in series A the nitric acid contained a uniform amount, about 3% by volume, of added water; and in Series B it contained another common amount, about 5% by volume, of water (the exact proportions are noted in the Table).

FIG. 18.

Effect of nitrous acid on first-order rate of nitration of nitrobenzene in slightly aqueous nitric acid at −13·3°.



(× = *Points derived from Fig.* 13.)

The principal effect of these additions of water on the kinetic behaviour of nitrous acid is that they greatly reduce the range of concentration of nitrous acid over which anything approaching a linear relation holds between the reciprocal of the rate constant and the square-root of the nitrous acid concentration; and that they bring in at low concentrations that strong and rapidly intensifying anticatalytic effect, which in the absence of water becomes prominent only at considerably higher nitrous acid concentrations. This may be illustrated by the representation of the results of Table XXIV given in Fig. 18. We see here two strongly curved graphs, one for each water concentration, of the reciprocals of the rate constants against the square-roots of the nitrous acid concentrations. Actually, these graphs are cubic in form, as we shall note in more detail in Section (4.2.2). The nearly horizontal straight line at the bottom of the diagram shows, for comparison, the kinetic effect of nitrous acid in anhydrous nitric acid: this line is reproduced from Fig. 17. It will be evident that the general influence of added water is to make nitration much more sensitive to anticatalysis by nitrous acid; and that, in the presence of 3% or 5% of water, practically the whole of the observed anticatalysis is of that strong and rapidly steepening kind, which in other cases appears only at the higher concentrations of nitrous acid.

(4·2) *Discussion (Part IV): Nitrous Acid Effects: Oxides of Nitrogen as Electrolytes*

(continued from p. 2430).

(4·2·1) *Anticatalysis by Nitrous Acid in Low Concentration: Ionisation of Dinitrogen Tetroxide.*—One of the more easily controlled ways of preparing solutions in nitric acid of what we call nitrous acid is to dissolve (below 0°) a known weight of pure dinitrogen tetroxide (redistilled in oxygen) in pure nitric acid (freed from nitrous acid and water by distillation from sulphuric acid at low pressure); water may be added if required. The solutions prepared from these pure, colourless, materials are yellow, and spectrally, and in other respects, are indistinguishable from "yellow nitric acid," containing the same analytical amount of nitrous acid and the same amount (if any) of water, obtained in other ways, *e.g.*, by the thermal or photochemical decomposition of nitric acid (as in storage), or by the addition to nitric acid of nitrogen oxides lower than dinitrogen tetroxide. The state of oxidation of the species collectively regarded as nitrous acid, in whatever forms they may have been introduced, is

determined by the nitric acid medium, and, in nearly pure nitric acid, is essentially that of dinitrogen tetroxide. The problem of the nature of nitrous acid in solvent nitric acid can thus be simplified to that of determining the condition assumed by introduced, pure, dinitrogen tetroxide.

Although dinitrogen tetroxide is very soluble in anhydrous nitric acid, the solutions have a definite partial vapour pressure of the equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide. Hence one of the forms of change undergone by dinitrogen tetroxide in solvent nitric acid must certainly be partial homolytic dissociation to nitrogen dioxide. The yellow colour of the solutions suggests the presence, in small concentration, of nitrogen dioxide. It is true that the absorption of light by such solutions in the violet and near ultra-violet regions is not quite identical in spectral form with that of gaseous nitrogen dioxide; but the differences are probably not greater than could plausibly be explained by the polarising effect of solvation.

Reed has studied the electrical conductivity of solutions of dinitrogen tetroxide in nitric acid solvents. His measurements show that dinitrogen tetroxide is a definite electrolyte in such solvents. In pure nitric acid it is quite a strong electrolyte. But in solutions of nitric acid in excess of nitromethane, dinitrogen tetroxide becomes a typical weak electrolyte, obeying Ostwald's dilution law, and thus showing itself to be a binary electrolyte. As to the nature of the formed ions, Goulden and Millen have made it clear that they are nitrosonium and nitrate ions. They have studied the Raman spectra of solutions of dinitrogen tetroxide in nitric acid, and also the transport phenomena and electrode processes associated with their electrolysis. They have also noticed that the addition of an alkali-metal nitrate to a solution of dinitrogen tetroxide in nitric acid produces a marked increase in the partial vapour pressure of nitrogen dioxide and dinitrogen tetroxide, and in some conditions leads to a visible evolution of these gases. The spectroscopic evidence is given by Goulden and Millen in an accompanying paper (*J.*, 1950, paper no. 511), but their electrochemical work and Reed's is being continued in various directions, the intention being to publish the whole of this branch of the general investigation later.

From this work it follows that we have to picture dinitrogen tetroxide as undergoing, not only a homolytic, but also a heterolytic, dissociation in nitric acid:

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The total evidence strongly suggests that, in such conditions as are of present concern to us, the principal entity present is still the dinitrogen tetroxide molecule, although in nearly pure nitric acid large concentrations of the ions are produced.

In this respect, as in many others, we find solvent nitric acid exhibiting a character intermediate between that of sulphuric acid and that of relatively weakly polar or non-polar organic solvents. In two other papers of the present collection (*J.*, 1950, papers nos. 499, 508) it is shown, both cryoscopically and spectroscopically, that the splitting of dinitrogen tetroxide in sulphuric acid is entirely heterolytic. In non-polar solvents the fission is wholly homolytic. In nitric acid we observe both types of fission. Again, in sulphuric acid no molecular dinitrogen tetroxide survives, the heterolysis being complete. In organic solvents the heterolysis is vanishingly small. In nitric acid it is considerable, but still partial.

Turning to the kinetic findings, let us first consider Benford and Ingold's results (Part I) concerning zeroth-order nitrations in nitromethane. They observed that nitrous acid retarded these reactions in such a way that the reciprocal of the zeroth-order rate constant increased linearly with the square-root of the analytically determined concentration of nitrous acid. Now one molecule of nitrous acid is the analytical equivalent of one molecule of dinitrogen tetroxide. Since the principal solute species in Benford and Ingold's conditions was undoubtedly molecular dinitrogen tetroxide, we can take the concentration of this to be given, in sufficient approximation, by the analytically determined concentration of nitrous acid. Provided that, as the physical evidence indicates, the amount of nitrate ion formed by heterolysis of this dinitrogen tetroxide is considerably greater than the amount arising by self-ionisation of the nitric acid contained in the nitromethane solvent, equilibrium (23) will require the *total* concentration of nitrate ions to be approximately proportional to the square-root of the concentration of molecular dinitrogen tetroxide, and therefore approximately proportional to the square-root of the analytically determined concentration of nitrous acid. But we have already seen [Section (2.2.2)] that, within appropriate ranges of concentration, added nitrate ions retard zeroth-order nitrations in such a way that the reciprocal of the rate constant increases linearly with the first power of the concentration of nitrate ions. And we have seen also [Section (2.4.1)] that this can be understood on the basis that the effect of the nitrate ion is to deprotonate the nitric acidium ion in accordance with the reversible equation

(24), thus reducing the equilibrium concentration of nitric acidium ion, to which the rate of formation of nitronium ion, and hence the zeroth-order rate of nitration, is proportional:

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Combining these points, we see that nitrous acid should retard nitration in such a way that the reciprocal of the zeroth-order rate constant increases linearly with the square-root of the analytically determined concentration of nitrous acid. Thus, Benford and Ingold's law for the anticatalysis by nitrous acid of zeroth-order nitrations in nitromethane becomes explicable on the simple ground that "nitrous acid" exerts its effect by supplying nitrate ions as represented in equation (23), and that the nitrate ions act, as we have other reasons for believing they do, by deprotonating the nitric acidium ion in accordance with equation (24).

The analogous reciprocal-square-root law, which we have observed for the effect of nitrous acid on first-order nitrations, can evidently be explained on similar lines: the difference is only that the equilibrium concentration of nitric acidium ion now determines the stationary concentration of the nitronium ion, to which the first-order rate constant is proportional.

For first-order nitrations in anhydrous nitric acid as solvent the anticatalysis by nitrous acid is relatively weak: it is too weak to enable a chemically significant law for the effect to be critically derived from the data. The comparative weakness of the effect undoubtedly arises from a less favourable relation in nitric acid alone than in solutions of nitric acid in organic solvents, between the amounts of nitrate ion supplied by heterolysis of the dinitrogen tetroxide and the quantities funished by self-ionisation of the nitric acid. For this reason, the law obeyed by the effect is not expected to have any simple mathematical form.

(4.2.2) *Anticatalysis by Nitrous Acid in Higher Concentration and in the Presence of Water: Ionisation of Dinitrogen Trioxide.*—The substance of our theory of the specially strong anticatalysis of nitration by nitrous acid in the higher range of concentrations investigated, and by nitrous acid at all concentrations in the presence of suitable amounts of water, is that these effects arise from the formation of dinitrogen trioxide, which, although in smaller concentration than the dinitrogen tetroxide, is specifically a much more powerful anticatalyst.

When pure dinitrogen trioxide (redistilled in nitric oxide) is added to a large excess of absolute nitric acid at $-40°$, the blue colour of the former substance is instantly destroyed, and a yellow solution results which is quite similar to the solutions which one prepares by the use of dinitrogen tetroxide. The oxidation–reduction which this colour change indicates must in principle be a balanced reaction:

$$N_2O_3 + 2HNO_3 \rightleftharpoons H_2O + 2N_2O_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

It is undoubtedly true for the conditions of main concern to us that, of all the species collectively estimated as nitrous acid, the preponderating species is molecular dinitrogen tetroxide. This being so, it follows from an application of the mass law to equation (25) that the proportion of so-called nitrous acid which exists in the form of dinitrogen trioxide must increase with the total concentration of dinitrogen tetroxide, *i.e.*, of analytical nitrous acid, and also with the concentration of water. Up to the highest concentrations of nitrous acid, and of water, with which we deal in this paper, say, **M/3** for nitrous acid and **3M.** for water, the proportion of dinitrogen trioxide in the nitric acid solvents seems to be too small to permit estimation of the trioxide, in the presence of accompanying substances, by means of its colour, *i.e.*, by its absorption of light in the red and the near infra-red regions. However, when much more water is introduced into these solutions, they become blue. There can be no reasonable doubt that in such conditions important quantities of dinitrogen trioxide are formed, illustrating the reversibility of reaction (25).*

Let us now consider how dinitrogen trioxide might retard nitration with such specific strength that it can become effective as an anticatalyst at some quite low threshold of concentration.

We know many close analogies of chemical behaviour between dinitrogen trioxide and dinitrogen tetroxide. In the gas phase, and in non-polar or weakly polar organic solvents, dinitrogen trioxide is partly homolysed into nitric oxide and nitrogen dioxide, just as dinitrogen

* It is often assumed that molecular nitrous acid, HNO_2, is blue, but we doubt this: molecular nitrous acid should be pale yellow. We think that the blue colour attributed to nitrous acid is the property of its anhydride, with which the acid enters into equilibrium, even in the presence of much water. It is also stated that methyl nitrite is blue, but it should not be, having no suitable chromophore. And, in fact, it is not: prepared in these laboratories by Dr. A. T. Austin, it is pale yellow (and, according to his observation, it boils at $-18·5°$, not $-12°$ as is recorded in the literature). The blue colour observed by other workers is undoubtedly due to contamination by dinitrogen trioxide.

tetroxide in such conditions is partly dissociated into two molecules of nitrogen dioxide. Again, as is shown in two of the accompanying papers (*J.*, 1950, papers nos. 499, 508), dinitrogen trioxide, like dinitrogen tetroxide, is heterolytically dissociated in solvent sulphuric acid. The products of heterolysis in the two cases are strictly analogous, and for both oxides the heterolysis is complete. We shall now assume that analogies, such as we observe in non-polar and weakly polar solvents, on the one hand, and in highly polar sulphuric acid, on the other, will continue to hold in the solvent of intermediate character, nitric acid. In particular, we shall assume that, in solvent nitric acid, dinitrogen trioxide, just like dinitrogen tetroxide, will undergo partial homolysis and partial heterolysis side by side. This is expressed in equations (26), which are to be compared with equations (23):

$$NO + NO_2 \rightleftharpoons N_2O_3 \rightleftharpoons NO^+ + NO_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The products of the heterolysis will be the nitrosonium ion and the nitrite ion, and it is with the latter that we shall now be especially concerned.

Our theory is that, just as the anticatalytic behaviour of dinitrogen tetroxide is dependent on its heterolysis to the nitrate ion, so the retarding effect of dinitrogen trioxide arises from its heterolysis to the nitrite ion; and that the nitrite ion exerts its action, exactly as the nitrate ion does, namely, by deprotonating the nitric acidium ion. Accordingly, in the presence of dinitrogen trioxide, and therefore of nitrite ion, the stationary concentration of nitric acidium ion is limited by equilibrium (27):

$$HNO_3 + HNO_2 \rightleftharpoons H_2NO_3^+ + NO_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

This equilibrium will therefore limit zeroth-order and first-order nitration rates, both of which are proportional to the stationary concentration of nitric acidium ion.

Equation (27) is to be compared with equation (24), which expresses the analogous reaction of the nitrate ion. However, the nitrite ion, as the anion of a weak acid, will be a much stronger base than is the nitrate ion. Consequently, we must expect a low concentration of nitrite ion to be as effective as a much higher concentration of nitrate ion for the destruction of the nitric acidium ion, and hence for the anticatalysis of nitration.

Let us now combine equations (23), (25), and (26) in the following scheme:

$$\begin{array}{ccccc} NO_2 + NO & & & & 2NO_2 \\ \rightleftharpoons & & & & \rightleftharpoons \\ & N_2O_3 + 2HNO_3 & \rightleftharpoons & H_2O + 2N_2O_4 & \\ \rightleftharpoons & & & & \rightleftharpoons \\ NO_2^- + NO^+ & & & & 2NO^+ + 2NO_3^- \end{array} \quad . \quad . \quad (28)$$

It has to be emphasized that, under the conditions of our kinetic experiments, the equilibria of system (28) lie in the direction of dinitrogen tetroxide rather than dinitrogen trioxide, and of nitrate ions rather than nitrite ions. Obviously the ratio of nitrite ions to nitrate ions in a large excess of nitric acid must always be small. But the points of kinetic importance are, first, that, because of the superior specific effectiveness of the nitrite ion, a small ratio of nitrite to nitrate may well be large enough to give to the nitrite ion a practical kinetic importance; and secondly, that the ratio can be substantially increased by increasing either the concentration of the dinitrogen tetroxide (*i.e.*, of the nitrous acid as measured analytically) or the concentration of the water.

Therefore we can understand what happens to the total anticatalytic effect of nitrous acid as the concentration of analytical nitrous acid, or the concentration of water, is progressively increased. We deduce that, as the rising proportion of nitrite ion reaches some quite low threshold, this ion will begin to take a part in the anticatalysis quantitatively comparable to the part taken by the nitrate ion, which up to that stage had been the sole effective agent; and that, if the concentration of the analytical nitrous acid, or of the water, is further increased, so that the proportion of nitrite ion continues to rise, then this ion will rapidly assume a dominating rôle, with the result that the total anticatalytic effect will increase steeply. This is what we observe. It should apply alike to zeroth- and first-order nitrations, and, as far as our observations extend, it does so.

The confirmation of this interpretation on quantitative lines can readily be carried to a semi-quantitative stage, but hardly beyond that on the basis of our results. With the help of the mass-law, it is easy to derive mathematical expressions for the anticatalysis, which should have approximate validity over a considerable part of the investigated range of concentration. Thus we can deduce the equation $1/k_0 = a_0 + b_0[HNO_2]^{1/2} + c_0[HNO_2]^{3/2}$ for zeroth-order

nitration, and a similar formula for first-order nitration. In these equations the interesting term is the last, since it expresses the presumed effect of the nitrite ions.*

Equations of the type indicated have been found to have a considerable measure of validity when applied to our data. Thus in Fig. 18 (p. 2434), the curve labelled "5% H_2O," although it is scarcely distinguishable from the best smooth curve through the observational points, was actually drawn as the graph of the equation $10^{-3}k_1^{-1} = 0{\cdot}5 + 40[HNO_2]^{3/2}$. Similarly the curve labelled "3% H_2O," though it appears to be drawn to fit the points, is, in fact the graph of the equation $10^{-3}k_1^{-1} = 0{\cdot}3 + 25[HNO_2]^{3/2}$. It will be noticed that the ratio of the coefficients, 40 and 25, of the main terms in these equations is approximately equal to the ratio of the corresponding water concentrations—as one might expect from elementary theory.† We do not wish to over-emphasize such comparisons with experiment, because experimental error, the number of disposable constants, and the neglect of activity corrections, all limit their quantitative significance. However, considered as a semi-quantitative check, the above comparison is clearly satisfactory.

(5) Experimental Methods.

(5.1) *Purification of Materials.*

(5.1.1) *Nitric Acid.*—This was purified as described by Benford and Ingold (Part I), except that the two distillations from excess sulphuric acid were, by the use of a rotary oil-pump, conducted at lower pressures than they employed, and at temperatures below 0°. The second distillation was accomplished without permitting visible boiling. The colourless crystalline distillate was collected at −80°. It could be preserved in sealed tubes in the dark at −80°. It melted to give a colourless liquid, which had the theoretical acid equivalent of nitric acid to within the error of measurement. Its content of nitrous acid was often undetectably small, and was normally less than 0·001M. At temperatures above 0° the material developed nitrous acid rapidly.

(5.1.2) *Organic Solvents.*—Specimens of nitromethane obtained from several commercial sources, and also samples prepared in the laboratory, were dried ($CaCl_2$), and distilled through an efficient fractionating column, the constant-boiling fraction (*e.g.*, of b. p. 101·2°/762·0 mm.) being collected for use.

Acetic acid ("AnalaR" supplied by British Drug Houses Ltd.) was boiled for several hours under reflux with chromium trioxide, and recovered by distillation. It was then rectified with the aid of a fractionating column, a fraction of b. p. 117·8—118·2° being collected for further purification. This was fractionally frozen until the m. p. 16·65° was obtained. The correct weight of water was then added in order to produce the 99·8% acetic acid used as solvent.

(5.1.3) *Nitrates and Other Salts.*—All the salts employed, *viz.*, lithium, sodium, potassium, ammonium and urea nitrates, potassium perchlorate, and potassium hydrogen sulphate, were purified by crystallising them several times from water, and drying them at temperatures between 110° and 200° in a vacuum over phosphoric oxide.

(5.1.4) *Dinitrogen Tetroxide and Dinitrogen Trioxide.*—The procedures used for the preparation and purification of these substances were as described in an accompanying paper (*J.*, 1950, paper no. 499).

(5.1.5) *Aromatic Compounds.*—All the compounds employed for nitration, *viz.*, benzene, toluene, ethylbenzene, *p*-xylene, mesitylene, fluoro-, chloro-, bromo-, and iodo-benzene, *o*-, *m*-, and *p*-dichlorobenzene, 1 : 2 : 4-trichlorobenzene, ethyl benzoate, nitrobenzene, *p*-chloronitrobenzene, and 1-nitroanthraquinone, were purified by the standard methods of fractional freezing, crystallisation from solvents, sublimation, or distillation through an efficient fractionating column. Some of the substances were given additional special treatments. For instance, benzene was shaken with sulphuric acid until the latter ceased to become coloured, and toluene was shaken with mercury.

(5.2) *Methods for following the Kinetics of Nitration.*

(5.2.1) *The Dilatometric Technique.*—The technique used was essentially that worked out by Benford and Ingold (Part I). The instruments employed, *viz.*, the precision thermostats, including one for temperatures below 0°, and the tapless dilatometers, were as described by them.‡ Difficulty with

* The power 3/2, characterising this term, arises as follows. The use of the mass law, with reference to equations (28), yields the conclusion that the product $[NO^+][NO_3^-]$ is proportional to $[N_2O_4]^{\frac{1}{2}}$; and that $[NO^+]$, which is approximately equal to $[NO_3^-]$, is therefore proportional to $[N_2O_4]^{1/2}$. Thus $[NO_3^-]$ becomes proportional to $[N_2O_4]^{3/2}$, that is, to $[HNO_2]^{3/2}$, where HNO_2 signifies the *analytical* nitrous acid.

† The theory is as follows. With reference to equations (28), the mass law indicates that the product $[NO^+][NO_3^-]$ is proportional to $[H_2O]$, and that the product $[NO^+][NO_3^-]$, and hence also each of its nearly equal factors, are independent of $[H_2O]$. Thus $[NO_3^-]$ becomes proportional to $[H_2O]$, justifying the statement in the text. Of course, this applies only so long as there is too little water to produce important amounts of $[NO_3^-]$ by the ordinary aqueous ionisation of nitric acid.

‡ The most suitable of Benford and Ingold's dilatometers for use with rapid reactions is their "Type C," one limb of which is bent over for convenience in filling. However, occasionally during a run, a small droplet, formed by drainage of the capillary walls, gets into the down-facing end, thereby creating a pressure change which interferes with the hydrostatic equilibrium governing the relation between the heights of the two meniscuses in the body of the dilatometer. The possibility of this occurrence is excluded by making the bent-over part of the capillary tube detachable, through the provision, near the top, of a very small, ground-glass joint: then, as soon as the dilatometer is filled, the bend can be taken off.

maintenance of accurately constant temperatures over long periods was reduced by the use of thermostat regulators having closed heads filled with hydrogen. A cathetometer was employed for reading the dilatometers, greater accuracy being thus obtainable than could be secured by the use of a scale attached to the dilatometer.

Benford and Ingold's procedure for starting runs was slightly modified. The aromatic compound was weighed into a measuring flask, which was immersed in the thermostat. The nitrating medium contained in another flask was also placed in the thermostat, and was there allowed to come to thermal equilibrium. It was then added to the aromatic compound up to the marked volume (10 c.c.), and simultaneously the stop-watch was started. The mixture was immediately shaken until homogeneous; it was then transferred, with the aid of a suction pump, to the dilatometer, likewise immersed in the thermostat.

In a few cases the thermal effect of dissolving the aromatic compound in the nitrating medium was investigated with the aid of a thermocouple. Increases of temperature, extending to 2·4° in the more concentrated solutions, were observed; but in the dilatometers all these disturbances disappeared in less than 5 minutes.

(5) 22. *Chemical Control of Dilatometric Runs.*—When following reaction kinetics by the variation of a physical property, it is important to identify the reaction measured. In the present work, this was done, for each aromatic compound and each nitrating medium, by at least one of the following four methods, *viz.*, (1) by determining aromatic nitroxyl in the product after the dilatometric contraction ceases; (2) by isolating, and obtaining an ultimate analysis of, the nitration product after the contraction ceases; (3) by ascertaining that the mononitro-derivative of the aromatic compound used (or at least one of the nitro-isomerides, when there are several) does not give any dilatometric or other indication of reaction when placed for the same length of time under the same conditions; and (4) by following the kinetics of the reaction completely by chemical analysis.

Method (1) was used in every case. We do not quote the results, because they are numerous and quite uniform: always the percentage of nitroxyl corresponded to mononitration to within ±0·2%. Method (2) was employed occasionally as an additional check. Thus the product from 1 : 2 : 4-trichlorobenzene on analysis (Drs. Weiler and Strauss) gave the following figures: C, 32·4; H, 1·2; N, 6·3 (Calc. for $C_6H_2Cl_3O_2N$: C, 31·8; H, 0·9; N, 6·2%). Method (3) was often used as a further check, especially in cases of mixed-order kinetics, since it was then particularly necessary to be certain that the kinetic complications did not arise from consecutive reactions. Thus it was ascertained that, under the conditions used for the nitration of chlorobenzene, *p*-chloronitrobenzene undergoes no change. Method (4) was employed only as an approximate check on the dilatometric results for some fast nitrations of nitrobenzene in absolute nitric acid. These runs involved the difficulty that the dilatometric rate constant depended on observation only over the latter part of the reaction, a good deal of reaction having occurred during the few minutes in which the thermal effect of mixing precludes dilatometric readings of the reaction rate. However, the heat of mixing has a much less serious effect on the reaction rate itself than on its dilatometric indication, and thus in principle the rate can be measured in other ways, at least approximately, during much of the period of the thermal disturbance. We stopped the nitrations by delivering samples into water about once a minute, and then determined the dinitrobenzene in the diluted samples by a method involving the use of dimethylaniline, as described below.

(5.3) *Methods of Chemical Analysis.*

(5.3.1) *Determination of Nitroxyl.*—For the routine control of dilatometric runs by method (1) above, nitroxyl in the isolated aromatic nitration product was determined by the method of Kolthoff and Robinson (*Rec. Trav. chim.*, 1926, **45**, 169), 30% aqueous sodium nitrate being employed as buffer, and aqueous potassium thiocyanate as the indicator. The method was tested by its application to a considerable variety of pure nitro-compounds, including at least one isomeric form of all those which were expected to be produced by nitration. In almost all cases the results were correct to within 0·2%. The one exception was *m*-nitroanisole which, because of an impurity, persistently gave results 0·4% high.

In the chemically followed kinetic runs on the nitration of nitrobenzene in absolute nitric acid, noted under method (4) above, we traced the production of the dinitrobenzenes by utilising the coloured molecular compounds which nitrobenzene and the dinitrobenzenes yield on combination with dimethylaniline (Biron and Morguleva, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1598). The intensity of the colour given by any of these nitro-compounds in a large excess of dimethylaniline is proportional to the concentration of the nitro-compound. The colour produced by nitrobenzene is pale yellow, whilst that given by the dinitrobenzenes is an intense red; and thus, by measuring the intensity of the red colour, it is possible to determine the dinitrobenzenes. Though the accuracy of the method is low, it was sufficient for the purpose we had in view, which was to confirm, in the case of these rapid nitrations, that the part of the reaction which could be followed dilatometrically was indeed a part of the mononitration process. Our method was to make the diluted samples alkaline and extract them with ether; and then, after drying and evaporating the ether, to make up to a fixed volume with dimethylaniline, and measure the intensity of the colour. This was done with the aid of a Spekker absorptiometer, employing green filters, which transmit only light which is not absorbed by the nitrobenzene compound but is absorbed by the dinitrobenzene compounds.

(5.3.2) *Determination of Nitrous Acid.*—Benford and Ingold (Part I, *loc. cit.*) developed a method for the determination of nitrous acid, which is based on an earlier method due to Lunge and Lwoff, and

consists in employing the nitrous acid for a diazotisation, and thence for the production of an azo-dye, which can be estimated colorimetrically. At first we used exactly Benford and Ingold's procedure, which involves, first, comparing in a colorimeter, against a permanent colour standard, the azo-colour developed from a series of nitrite solutions of known concentrations, and then, comparing the azo-colour developed from the solution to be analysed, in the same way, and against the same permanent colour standard.

With the higher colour intensities involved in some of these analyses we found difficulty in matching the colours. Our first reply to this was to go over to the volumetric method described below, but only for the determination of the higher nitrous acid concentrations, for which alone this method was satisfactory. The method of Benford and Ingold was retained for the determination of low concentrations.

The volumetric method is based on the oxidation of nitrous acid by chloramine-T. A measured amount of the solution to be analysed was made up to a known volume with water, and measured samples of the diluted solution were delivered into stoppered bottles, there to be mixed with more water, some glacial acetic acid, and measured amounts of a standard solution of chloramine-T. The mixtures were shaken, and, after 15—20 minutes, were treated with an excess of potassium iodide and titrated against standard thiosulphate, with starch as indicator. Blank experiments showed that no sensible error was caused by the presence of the aromatic compounds in some of the solutions analysed. The only serious disadvantage of this method is that, for low nitrous acid concentrations, the titre-differences are small, and the determinations correspondingly inaccurate.

At a later stage, we found it convenient to return to the colorimetric method, but in a modified form, which overcame the above-mentioned difficulty of colour matching at high colour intensities, and enabled both high and low concentrations of nitrous acid to be determined satisfactorily by a common procedure. The new method consisted in developing the azo-colours from the nitrous acid solutions just as before, and then measuring the colour intensity by means of a Spekker absorptiometer, without the employment of any permanent colour standard.

Green filters were used in order to secure strong absorption. The left-hand cell and one right-hand cell of the absorptiometer were filled with water, and the other right-hand cell with a solution containing the azo-compound. The diaphragm was closed, and the drum set to zero, with the two water cells in line; and the sensitivity of the galvanometer was then adjusted to give a full scale deflection. The cell containing the azo-colour was now substituted for the water cell on the right-hand side of the instrument, and the diaphragm was opened until the galvanometer showed no deflection. Then the water cell on the right-hand side was restored to its original position, and the resulting galvanometer deflection was reduced to zero by rotation of the calibrated drum. The instrument was first calibrated by this means, a number of nitrite solutions of known concentration being used for the purpose; and a curve was constructed connecting the drum reading with the concentration of nitrous acid. It was then necessary only to repeat the procedure with the solution to be analysed, note the drum reading, and apply the calibration curve.

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494. *Kinetics and Mechanism of Aromatic Nitration. Part III. Nitration in Acidified Aqueous Nitric Acid.*

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The nitration of 2-phenylethylsulphonic acid, and of benzylsulphonic acid, in aqueous solutions of nitric acid, containing some perchloric or sulphuric acid, has been kinetically studied. It is made plausible that the sulphonic acids are nitrated through their anions, which are comparable in reactivity to some of those aromatic compounds which exhibit zeroth-order nitration in organic solvents (cf. Part II, Section 1). With Millen, it is spectroscopically established that, in the aqueous media used, the perchloric acid is completely, and the sulphuric acid largely, ionised, whilst the nitric acid exists almost wholly in its non-dissociated form. It is shown that in these media the nitrations uniformly follow a first-order law. The effect of medium composition on the reaction rate is characterised by rather narrow thresholds, across which the nitrations pass, from being very slow, to very fast. An increase of the concentration either of nitric acid, or of the added strong acid, the concentration of the other being suitable, will lead to these thresholds of onset of nitration, which can arise in the presence of, *e.g.*, 75 mols. % of water. In the neighbourhood of such a threshold, added sodium perchlorate accelerates, whilst added sodium or ammonium nitrate retards, nitration.

The thresholds show that the nitrating agent in these aqueous nitrations is not the nitric acid molecule, the concentration of which changes relatively slowly with changing composition of the medium. It could be the nitric acidium ion, $H_2NO_3^+$, the equilibrium degree of formation of which is likely to exhibit thresholds, owing to a diversion of the proton, which is lost by the strong acid, from uptake by water towards uptake by nitric acid, as the activity of the water falls below a more or less critical value in consequence of a progressive involvement of the water in hydrates. The accelerating effect of sodium perchlorate is regarded as a general salt effect, operating by reduction of the water activity as the result of an increased formation of ion hydrates. The retarding effect of sodium or ammonium nitrate is considered to be the overall result of this accelerative general salt effect, and of a more powerful, specific, retarding effect of nitrate ions, which are assumed to act by deprotonating the nitric acidium ion (cf. Part II, Section 2). No evidence has been found that nitronium ions are effective in these solutions, in which they may not be able to exist in sufficient concentration, though the possibility of their intervention in such conditions is not excluded.

(1) *Chemical Conditions in Aqueous Nitration.*

(1.1) *Existence of the Nitric Acidium Ion.*—The kinetic observations reported in Part II provide the first definite proof of the existence of the nitric acidium ion, $H_2NO_3^+$, inasmuch as they show that its reversible production from nitric acid constitutes the first of the two steps by which the nitronium ion is formed in nitric acid:

$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental evidence was concerned with aromatic nitration by nitric acid in constant excess in organic solvents such as nitromethane and acetic acid. It could be shown by reference to the changes in kinetic order that, under these conditions, the nitrating agent was always the nitronium ion. There were two limiting kinetic types of nitration, the first-order and zeroth-order types the former applying to the less reactive aromatic compounds, such as di- and tri-halogenobenzenes, and the latter to the more reactive compounds, such as benzene and toluene. It was found that nitration, in both these kinetic forms, was strongly accelerated by the addition of small amounts of an acid stronger than nitric acid, and was strongly retarded by the addition of small concentrations of nitrate ions; and that both these effects on rate took place without disturbance to the reaction order, even when this was of zeroth order. Comparably small concentrations of added water had practically no effect on the rate.

These results show that the production of nitronium ion involves both the uptake by nitric acid of a proton, and the elimination from nitric acid of a nitrate ion. The effect of adding small amounts of an acid stronger than nitric acid is to increase the proton uptake by a generalised form (1•) of reaction (1):

$$HNO_3 + HX \rightleftharpoons H_2NO_3^+ + X^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1•)$$

The effect of adding nitrate ions is to reverse the reaction stage (1) in which nitrate ion is produced. And since these effects, the second in particular, apply to zeroth-order nitrations, the stage reversed (1) cannot be that in which the nitronium ion is produced (2), because it is essential for zeroth-order nitration that nitronium ion production should not be appreciably reversed, *i.e.*, that substantially all the formed nitronium ion should combine with the aromatic

compound. This proves the two-stage nature of the process, and the intermediate formation of the nitric acidium ion.

(1.2) *Possible Nitrating Agents in Aqueous Nitric Acid.*—Water is in a different case from the nitrate ion. Water is not produced simultaneously with the nitric acidium ion in reaction-stage (1). It is consistent that in zeroth-order nitration its retarding action is trivial in comparison with that of the nitrate ion. On the other hand, water is produced simultaneously with the nitronium ion in reaction-stage (2); and thus the addition of *enough* water should cause reversal of that reaction stage. Therefore, if we are observing a zeroth-order nitration of one of the more reactive aromatic compounds, the addition of sufficient water should retard the reaction, and should change the zeroth-order kinetics into first-order kinetics; for first-order nitration by nitronium ion results when nearly all the formed nitronium ion goes back into what it came from, only a small proportion combining with the aromatic compound.

This presupposes that, in the presence of much water, nitration continues to take place through the nitronium ion. However, it can be imagined that the water added might be sufficient completely to destroy the nitronium ion, leaving the possibility of nitration through the presumably less reactive nitric acidium ion. Any such nitration also should have a reduced speed, and should be kinetically of the first order. The latter conclusion follows because the nitric acidium ion can safely be assumed to be destroyed much more rapidly by the proton transfer which reverses the process of its formation (reaction 1 or 1*) than it will be by combination with an aromatic molecule.

It is difficult to distinguish between these two possible mechanisms, *viz.*, (*a*) nitration by the extremely minute amounts of nitronium ion that might survive in equilibrium with a great excess of water, and (*b*) nitration by larger equilibrium amounts of nitric acidium ion in these conditions. We have not succeeded in devising a critical experimental distinction. However, as has already been reported in a preliminary way (*Nature*, 1946, **158**, 514), we have studied the kinetics of aromatic nitration under conditions which are calculated very strongly to repress nitration by the nitronium ion, and to favour to the greatest possible extent nitration by the nitric acidium ion.

(1.3) *Entities Present in the Nitrating Solutions.*—In this work, the organic solvent of the experiments of Part II has been replaced by water. This was done in order to destroy the nitronium ion as completely as possible. And the aqueous solutions have been acidified with a very strong acid, usually perchloric acid, in order to increase the production of nitric acidium ion. A typical composition of a nitrating solution would contain 70—75 mols. % of water, whilst of the remaining material usually more than half would be nitric acid and less than half perchloric acid. In some experiments a salt was added, such as sodium perchlorate, sodium hydrogen sulphate, sodium nitrate, or ammonium nitrate.

It is important to note that, in mixtures of this type, nitric acid is only slightly ionised as an acid. On the other hand, perchloric acid is completely dissociated. Its strong acidity is, no doubt, partly responsible for the relative lack of acidity of the nitric acid. Dr. D. J. Millen established for us the existence of these conditions by examining the Raman spectra of some typical nitrating mixtures. In illustration, one of his microphotometer records is reproduced in Fig. 1. It relates to the nitration solution which was made up for kinetic run No. 103, and which had the following molecular composition: H_2O, 72; HNO_3, 17; $HClO_4$, 11 mols. %.

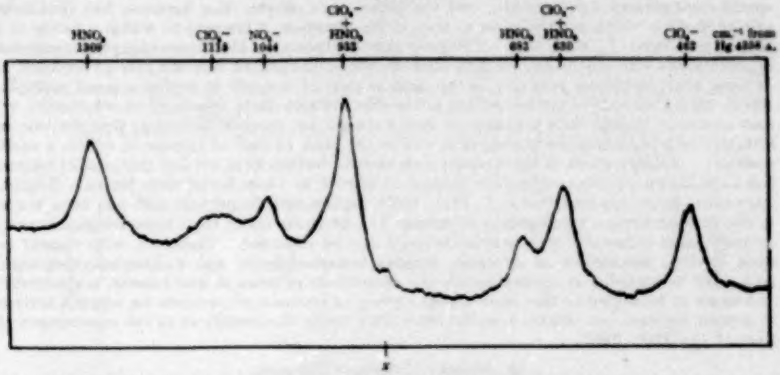
The Raman spectrum shows that the perchloric acid is completely converted into perchlorate ion: the spectrum of this ion is prominent, even the diffuse line around 1115 cm.$^{-1}$ (cf. Millen, *J.*, 1950, paper no. 509) being well recorded, whereas the characteristic spectrum of the perchloric acid molecule is entirely absent. On the other hand, the spectrum of the nitric acid molecule is strongly developed, whilst the spectrum of the nitrate ion is quite weak. Intensity measurements show that only 4% of the total nitric acid, *i.e.*, only 0·68 mol. % of the whole mixture, is in the form of nitrate ion.

No trace of the easily detectable nitronium ion line can be found in the spectrum. What the spectrum cannot tell us is how much of the nitric acid is ionised as a base to form nitric acidium ion. The 11 mols. % of hydrogen ions, split off from the perchloric acid, must have added themselves either to water molecules to form hydroxonium ions, or to nitric acid molecules to give nitric acidium ions; but we can find neither in the Raman spectrum. This is a well-known difficulty: no simple or substituted hydroxonium ion has yet been induced to yield a Raman spectrum. The generally accepted explanation, due to Bauer, is that such ions exchange their protons too frequently to yield well-defined vibrational energy levels.

The spectrum nevertheless establishes that a large proportion of the introduced nitric acid is present as nitric acid molecules. The 11 mols. % of hydrogen ions derived from the added

perchloric acid must be distributed in some unknown ratio between the water and the nitric acid; and, even if all the hydrogen ions should have added themselves to nitric acid, there would still be 5 mols. %, calculated on the total mixture, of surviving molecular nitric acid, out of the 17 mols. % of added nitric acid, since less than 1 mol. % is present as nitrate ion. This is important, because we shall show later that small changes in the composition of the nitrating solution, *e.g.*, the use of a little more or a little less perchloric acid, can make large changes in the rate of nitration, whereas it could not, under any hypothesis as to how the hydrogen ion is distributed between water and nitric acid, make large changes in the concentration of molecular nitric acid. From this we shall conclude that nitration by molecular nitric acid is not under observation in the present experiments.

FIG. 1.



Microphotometer record of part of the Raman spectrum of the nitration solution of Run No. 103. *Stokes lines excited by* Hg 4358 A. (*The perchlorate ion frequency* 935 *cm.*$^{-1}$, *excited by* Hg 4347·5 A., *can be seen at* x.)—By D. J. MILLEN.

Another conclusion towards which the spectral evidence helps is that, if nitration is by the nitric acidium ion, then this must be present in comparatively small concentration: it cannot result from a nearly complete addition of the hydrogen ions, derived from perchloric acid, to nitric acid rather than to water. For if it did, the concentration of nitric acidium ions would not be a particularly sensitive function of the analytical composition of the nitration mixture: it would, over considerable ranges, change proportionately to the introduced perchloric acid, whereas we shall find that the rate of nitration changes much more steeply.

In some experiments an aqueous sulphuric acid medium, instead of aqueous perchloric acid, was employed. Qualitatively the situation was similar: the sulphuric acid was largely ionised, whilst the nitric acid was present mainly, but not wholly, in its molecular form. This again was established by Dr. Millen's examination of the Raman spectra. However, these Raman spectra were unsuitable for intensity measurements, owing to overlapping of the relevant lines.

(1.4) *Reactivity of the Aromatic Compounds Nitrated.*—Some explanation is necessary concerning the choice of aromatic compounds for nitration in the conditions described. We did not regard the well-known aqueous nitration of phenol as providing evidence concerning general mechanisms of aromatic nitration in aqueous solution, because special mechanisms of nitration operate in the nitration of phenol and aniline and their derivatives. We were concerned with general mechanisms of nitration: mechanisms applying to particular types of compound seemed to us to need separate consideration afterwards (Parts VI—VIII, *J.*, 1950, paper no. 512 *et seq.*).

It was necessary to employ water-soluble aromatic compounds; we used 2-phenylethylsulphonic acid, and, to a smaller extent, benzylsulphonic acid. Ingold, Ingold, and Shaw have given evidence that the latter nitrates through its anion (*J.*, 1927, 813); and, having regard to the known effect of negative ionic charges in accelerating aromatic substitution, it seems highly probable that both these strong acids nitrate through their anions. (We always introduced

the acids as their sodium salts, supposing that in this form they would make the smallest initial disturbance to the concentration of hydrogen ions and of the other active components of the nitration medium.)

The rates of nitration of the two sulphonic acids have not yet been investigated by the competition method of Ingold and Shaw (*J.*, 1927, 2918); and therefore it is not known by direct observation where they stand, relatively to benzene itself and to other simple benzene derivatives, with respect to their reactivity in nitration. However, it is known that benzylsulphonic acid, on mononitration, gives 14% of the *m*-nitro-isomeride (Ingold, Ingold, and Shaw, *loc. cit.*), and that this proportion is not very different from those given by ethyl phenylacetate (11%) or benzyl chloride (15%) (Baker and Ingold, *J.*, 1927, 832; Flürscheim and Holmes, *J.*, 1928, 1611; Ingold and Shaw, *J.*, 1949, 575)—two compounds which have been investigated by the competition method. It has been shown that the former of the two compounds nitrates more quickly, and the latter more slowly, than benzene, but that both nitrate at rates which are the same as that of the nitration of benzene to within a factor of 4 (Ingold and Shaw, *J.*, 1949, 575). Using our general theoretical ideas concerning the connexion of orientation with reactivity, we may infer with some assurance that the rate of nitration of ionising benzylsulphonic acid will be the same as that of benzene to within a small multiple. Again, taking account of our knowledge of the effect of side-chain homology on orientation, we may conclude, though with a somewhat larger margin for possible deviation, that the rate of nitration of 2-phenylethylsulphonic acid will be the same as that of toluene to within a small multiple. A rough check on these conclusions may be derived from the fact that, whilst toluene has been shown by the competition method to nitrate 24 times faster than benzene (Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959), 2-phenylethylsulphonic acid has been found in the present kinetic investigation to nitrate 11—12 times faster than benzylsulphonic acid. A more exact numerical correspondence could not be expected. Therefore, with respect to their intrinsic reactivities in nitration, ionising benzylsulphonic and 2-phenylethylsulphonic acids may be regarded as approximately the equivalents of benzene and toluene, respectively, and hence as belonging to that more reactive group of aromatic compounds for which nitration in organic solvents can assume a zeroth-order form under the conditions of the experiments of Part II (*J.*, 1950, 2400).

(2) *Kinetics of Aqueous Nitration.*

(2.1) *General Form of Kinetics.*—As in the work described in preceding papers of this series, dilatometry has been the principal means by which the reaction kinetics have been followed in the study of nitration here reported. Chemical examination was used occasionally for checking the interpretation of the volume changes.

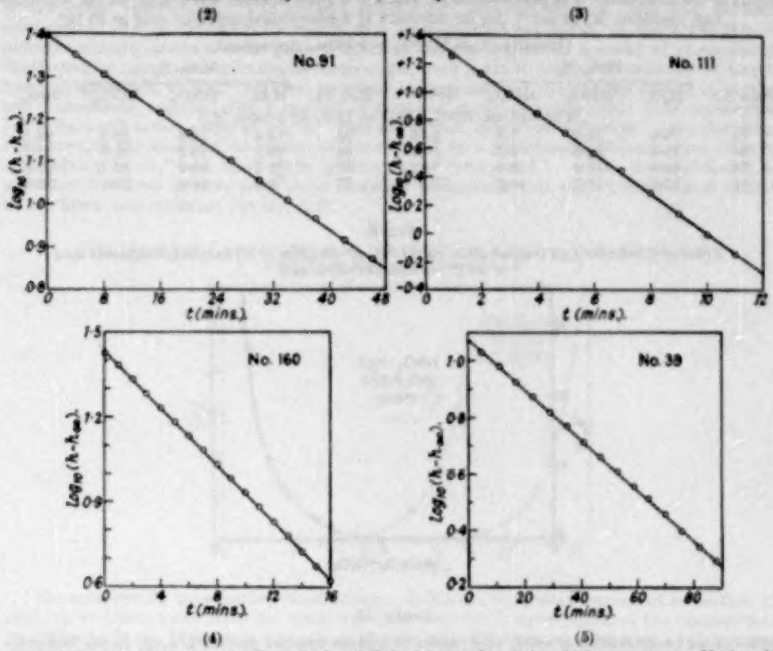
In the aqueous-acid solutions which have been employed for nitration in these experiments, the nitric acid was always present in constant excess over the aromatic compound. Under these conditions, the nitrations of both 2-phenylethylsulphonic acid and benzylsulphonic acid obey a first-order rate law with considerable accuracy. In illustration, Figs. 2—5 are given which show logarithmic plots of the variable part of the dilatometric height against time. The examples are chosen to illustrate the use of both the aromatic sulphonic acids, of both the added strong acids, of medium compositions distributed over the range of compositions investigated, and of added salts. First-order kinetics were invariably observed: a careful search was made for signs of the incursion of a zeroth-order process, but none could be found.

(2.2) *Effect of Medium Composition on Nitration Rate.*—The most salient feature of the connexion between the composition of the nitration medium, and the rate at which, at a fixed temperature, a given aromatic compound will be nitrated in it, is the existence of what may be called "thresholds" of reactivity in certain regions of composition. For instance, one may study the rate of nitration of a particular substance, at a fixed temperature, in an aqueous nitric acid of given concentration, to which progressively increasing amounts of perchloric acid are added; it is then found that no appreciable reactivity is developed until a certain stage is reached in the addition of the perchloric acid, but that, then, the reaction rate rises to very high values for quite small further increases in the content of perchloric acid.

Results are given in Table I for the first-order rate constants of nitration of 2-phenylethylsulphonic acid at 30·1° in a certain aqueous nitric acid (containing 18 mols. % of nitric acid and 82 mols. % of water), to which increasing proportions of perchloric acid were added. From the graph of the results, which is shown in Fig. 6, one sees that there exists a fairly narrow band of concentrations of perchloric acid, running from about 8 to about 11 mols. %, below which the reaction was too slow to be measured, whilst above it the reaction was too fast to be measured.

FIGS. 2—5.

Kinetic course of nitration by acid-aqueous nitric acid.



(2) Run No. 91. *Nitration of sodium 2-phenylethylsulphonate by nitric acid in aqueous perchloric acid. Medium :* H_2O, 76·5; HNO_3, 12·2; $HClO_4$, 11·3 *mols.* %. *Temp.* 30·10°. *Initially,* $[C_6H_5{\cdot}SO_3Na] = 0{\cdot}169$M. *From the graph* $k_1 = 0{\cdot}000445$ *sec.*$^{-1}$. *By Guggenheim's method,* $k_1 = 0{\cdot}000432$ *sec.*$^{-1}$.

(3) Run No. 111. *Nitration of sodium 2-phenylethylsulphonate by nitric acid in aqueous perchloric acid. Medium :* H_2O, 67·7; HNO_3, 25·5; $HClO_4$, 6·8 *mols.* %. *Temp.* 30·10°. *Initially,* $[C_6H_5{\cdot}SO_3Na] = 0{\cdot}169$M. *From the graph,* $k_1 = 0{\cdot}00530$ *sec.*$^{-1}$. *By Guggenheim's method,* $k_1 = 0{\cdot}00537$ *sec.*$^{-1}$.

(4) Run No. 160. *Nitration of sodium 2-phenylethylsulphonate by nitric acid in aqueous perchloric acid with added sodium nitrate. Medium :* H_2O, 72·6; HNO_3, 17·2; $HClO_4$, 10·2 *mols.* %. *Temp.* 30·10°. $[NaNO_3] = 0{\cdot}882$M. *Initially,* $[C_6H_5{\cdot}SO_3Na] = 0{\cdot}169$M. *From the graph,* $k_1 = 0{\cdot}00190$ *sec.*$^{-1}$. *By Guggenheim's method,* $k_1 = 0{\cdot}00187$ *sec.*$^{-1}$.

(5) Run No. 39. *Nitration of sodium benzylsulphonate by nitric acid in aqueous sulphuric acid. Medium :* H_2O, 74·3; HNO_3, 7·0; H_2SO_4, 18·7 *mols.* %. *Temp.* 39·96°. *Initially,* $[C_6H_5{\cdot}SO_3Na] = 0{\cdot}164$M. *From the graph,* $k_1 = 0{\cdot}000342$ *sec.*$^{-1}$. *By Guggenheim's method,* $k_1 = 0{\cdot}000333$ *sec.*$^{-1}$.

(We use ordinary logarithmic plots, such as are illustrated, for testing the degree of accuracy with which a first-order law is obeyed. But where the result of this test is satisfactory, we employ Guggenheim's method of plotting in order to derive the rate constant. Guggenheim's method was devised for the purpose of giving the best values of rate constants ; but it is not well suited for exhibiting small deviations from an integral reaction order.)

A similar effect was encountered when, starting with an aqueous perchloric acid of fixed concentration, progressively increasing amounts of nitric acid were added. The left-hand part of Table II contains a set of rate constants for the nitration of 2-phenylethylsulphonic acid at 30·1° in an aqueous perchloric acid (containing 9 mols. % of perchloric acid and 91 mols. % of water), with various proportions of added nitric acid. The right-hand part of the Table contains a similar set of figures relating to another aqueous perchloric acid (containing 13 mols. % of perchloric acid and 87 mols. % of water), along with added nitric acid. The rate graphs for these two sets of mixtures are in Fig. 7. Their difference of position illustrates another general

TABLE I.

Effect of the concentration of perchloric acid, added to a given aqueous nitric acid, on the first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of 2-phenylethylsulphonic acid at* 30·10°.

(Initially, $[C_6H_5SO_3Na] = 0{\cdot}169$M., throughout.)

Run No.	Mols. % H_2O.	Mols. % HNO_3.	Mols. % $HClO_4$.	10^4k_1.	Run No.	Mols. % H_2O.	Mols. % HNO_3.	Mols. % $HClO_4$.	10^4k_1.
(Throughout, $HNO_3 : H_2O = 18{\cdot}0 : 82{\cdot}0$ mols. %.)									
79	75·5	16·7	7·8	1·16	82	73·4	16·3	10·3	14·5
80	75·1	16·6	8·3	2·68	84	73·2	16·2	10·6	21·7
78	74·0	16·4	9·6	7·48	83	73·1	16·2	10·7	27·0
81	73·7	16·3	10·0	11·3	77	73·0	16·1	10·9	30·0

FIG. 6.

Effect of perchloric acid concentration on the rate of nitration of 2-phenylethylsulphonic acid at 30·10° *in aqueous nitric acid.*

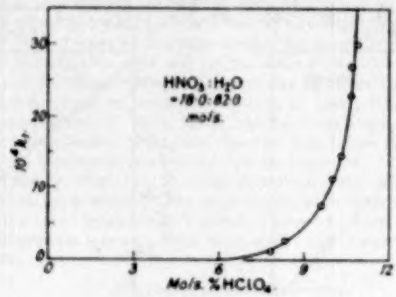


TABLE II.

Effect of the concentration of nitric acid, added to a given aqueous perchloric acid, on the first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of 2-phenylethylsulphonic acid at* 30·10°.

(Initially, $[C_6H_5{\cdot}SO_3Na] = 0{\cdot}169$M., throughout.)

Run No.	Mols. % H_2O.	Mols. % HNO_3.	Mols. % $HClO_4$.	10^4k_1.	Run No.	Mols. % H_2O.	Mols. % HNO_3.	Mols. % $HClO_4$.	10^4k_1.
(Throughout, $HClO_4 : H_2O = 9{\cdot}2 : 90{\cdot}8$ mols. %.)					(Throughout, $HClO_4 : H_2O = 12{\cdot}8 : 87{\cdot}2$ mols. %.)				
93	76·6	15·7	7·7	0·99	91	76·5	12·2	11·3	4·32
101	75·5	16·9	7·6	1·12	125	75·6	13·3	11·1	6·63
97	74·1	18·4	7·5	2·33	90	75·6	13·3	11·1	6·83
94	72·7	19·9	7·4	4·30	89	74·9	14·1	11·0	9·33
100	72·0	20·7	7·3	6·33	88	74·0	15·1	10·9	15·2
99	71·3	21·5	7·2	7·18	87	73·5	15·7	10·8	19·7
139	70·9	21·9	7·2	9·88	86	73·2	16·1	10·7	23·2
98	70·7	22·2	7·1	11·7	85	72·8	16·5	10·7	28·7
95	69·7	23·2	7·1	18·7	103	72·5	16·9	10·6	33·0
102	69·6	23·4	7·0	21·2					
96	67·8	25·4	6·8	48·0					
111	67·7	25·5	6·8	53·7					

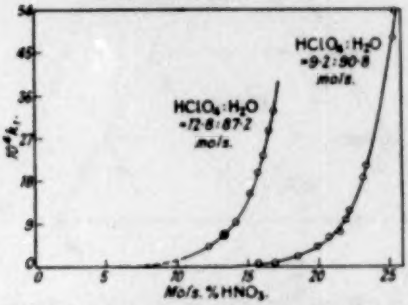
point, *viz.*, that the threshold of reactivity, as developed by the progressive addition of nitric acid, appears at a higher content of nitric acid the lower the proportion of perchloric acid in the original aqueous perchloric acid.

Similar thresholds are found when we keep the nitric and perchloric acids in a fixed ratio and dilute with increasing amounts of water. In this case we descend a steep curve qualitatively like those shown in Figs. 6 and 7, thereby passing, for a relatively small change of composition, from reactions which were too fast to be measured to others which were too slow to be measured in our conditions.

Independently of which component of the medium is being added, the position of the rate threshold with respect to the concentration of the added compound depends on the proportions of the other components. The general relationship between reaction rate and medium composition may be expressed by means of a three-dimensional model, in which the rate is plotted vertically above a basal plane containing the two degrees of freedom of composition. Employing triangular co-ordinates of composition, such a model for the nitration of 2-phenylethylsulphonic acid at 30·1° has been constructed from sections such as the curves of Figs. 6 and 7 constitute, together with a number of scattered observational points. It is represented in the form of a contour map in Fig. 8. This shows that, as we travel "south" from the water apex towards the contours, we remain at "sea-level" for a considerable distance, then come to a "shelving beach," and then, quite quickly, to a "steep cliff." As to the mechanism of nitration, it follows directly from these threshold phenomena that the nitrating agent cannot be the nitric acid molecule (Section 1.3).

FIG. 7.

Effect of nitric acid concentration on the rate of nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous perchloric acid.

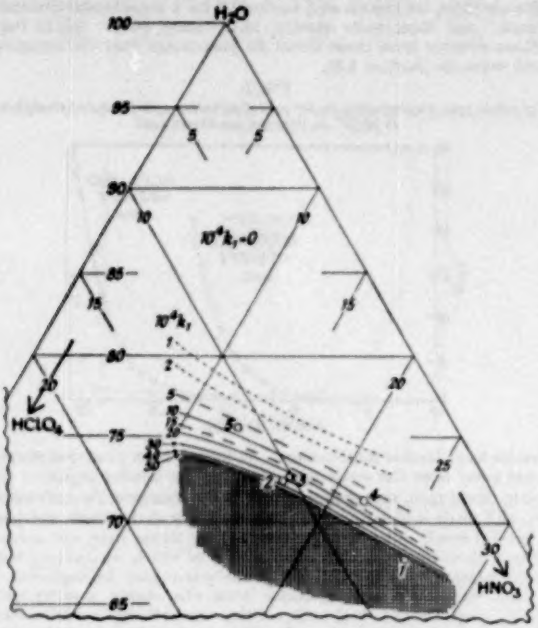


The same results have further implications. It follows from what was stated in Section 1.3 that, as we travel away from the water apex, towards the interior region of the composition–co-ordinate system, three main new species appear in the solutions, *viz.*, solvated hydrogen ions, perchlorate ions, and nitric acid molecules. Now we know that cations and positively charged centres are in general much more strongly solvated by water than are anions and negative centres. Therefore, in comparison with other effects of which we have to take account, the effect of the perchlorate ion on the activity of the water may be neglected. However, the hydrogen ion and the nitric acid molecule form the stable monohydrates, H_3O^+ and $H_3O \cdots HO{\cdot}NO_2$, respectively; and both entities can probably combine more loosely with additional water to form higher hydrates. It will be evident that the continued production of these hydrates, as protons derived from perchloric acid and as nitric acid molecules are progressively supplied to a fixed amount of water, must lead to a stage at which a relatively sharp decrease in the activity of the water will occur because a high proportion of the originally available water has already become bound in the hydrates present in such solutions. We assume that, so long as free water is in excess, most of the protons derived from perchloric acid will combine with water, rather than with nitric acid; *i.e.*, that, in these solutions, water will behave as a base which is at least as strong as nitric acid. We also adopt Gillespie and Millen's structure for nitric acid monohydrate (*Quart. Reviews*, 1948, **2**, 88) rather than Dalmon and Freymann's structure $HO{\cdot}NO_2 \cdots H_2O$: this is in accordance with the expectation that a moderately acidic molecule, such as nitric acid, should be hydrated mainly through its positive centre, *viz.*, its ionisable proton. The implication is that hydration, by partly neutralising the positive centre, must increase the basic strength of nitric acid. Therefore, as the water becomes progressively bound, the nitric acid being largely hydrated, there must be a shift in the relative efficiencies with which the two entities, water and nitric acid, compete for protons; and thus the above-mentioned sharp decrease in water activity will be accompanied by a similarly sharp increase in the proportion in which protons, derived from perchloric acid, will be bound by nitric acid. It is to this sharp increase in the formation of nitric acidium ion that we ascribe the observed sharp increase in nitration rate in the relevant region of composition.

(2.3) ***Effect of Added Salts on Nitration Rate.***—From the theory of the nitration process, it is to be expected that the addition of nitrate ions, in the form of sodium or ammonium nitrate, will reduce nitration rate; and that it will do this by reversing reaction (1) (cf. p. 2441), thereby diminishing the equilibrium concentration of nitric acidium ions.

FIG. 8.

Contour-map of relief model showing the effect of medium composition on the rate of nitration of 2-phenylethylsulphonic acid at 30·10°. (The significance of the points numbered 1—5 is explained in the text in connexion with Table III and Fig. 9—see pp. 2449 and 2450.)



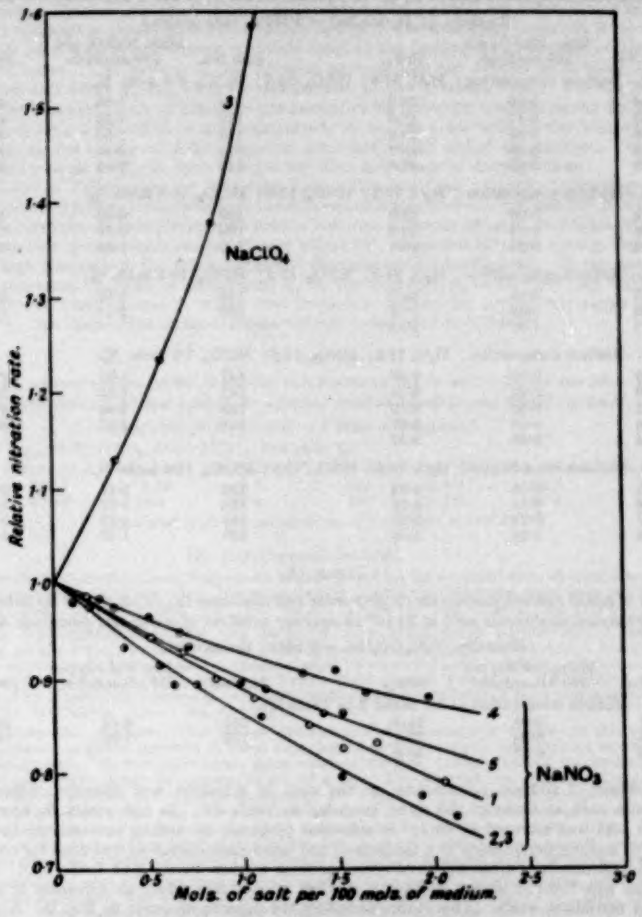
The same expectation follows, if we use our empirical knowledge (*a*) that, in the range of media investigated, the perchloric acid is completely dissociated, whilst the nitric acid is nearly completely undissociated; and (*b*) that the rate contours, over this range of media, lie, as Fig. 8 shows, more nearly normal to the co-ordinates of perchloric acid concentration than to the co-ordinates of nitric acid concentration. For the addition of, say, sodium nitrate must be the approximate equivalent, apart from any effect due to sodium perchlorate, of replacing an equimolecular amount of ionised perchloric acid by a corresponding quantity of non-ionised nitric acid; and this replacement is represented by a shift from left to right in Fig. 8; and therefore it must lead to a descent through the rate contours.

We have examined the effect of adding sodium or ammonium nitrate on the rates of nitration of 2-phenylethylsulphonic acid in a number of aqueous nitric acids containing either perchloric or sulphuric acid. In all cases the rates are decreased by the added nitrate. Some results concerning the effect of sodium nitrate on the first-order rate constants, measured at 30·10° in five aqueous solutions of nitric and perchloric acids, are given in Table III. The effect is illustrated by the graphs in the lower part of Fig. 9. Here, the rate constants for each group of experiments involving the same medium with different amounts of added salt, are expressed in terms of the rate in the salt-free medium as the unit.

The five groups of experiments are numbered 1—5 in Table III and Fig. 9, and the

FIG. 9.

Effect of added sodium nitrate and of added sodium perchlorate on the rate of nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous solutions of nitric and perchloric acids.



○ *Series* 1. ◑ *Series* 2. ◐ *Series* 3. ⊖ *Series* 4. ⊖ *Series* 5.

(*For medium compositions see Table III and Fig.* 8.)

compositions of the media, which were employed in them, are indicated by correspondingly numbered points in Fig. 8. It can be seen from Fig. 9 that the rate depressions caused by sodium nitrate vary with the medium, but lie within the range 6—14% for each 1 mol. % of added salt. These depressions are several times smaller than would be reckoned from the left-to-right rate-gradients of the relief model at the marked points in Fig. 8. This fact indicates the existence of a large positive salt effect due to sodium perchlorate.

TABLE III.

Effect of added sodium nitrate on the first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous solutions of nitric and perchloric acids.*

(Initially, $[C_6H_4{\cdot}SO_3Na] = 0{\cdot}169$M., throughout.)

Run No.	Mols. $NaNO_3$ per 100 medium.	10^4k_1.	Run No.	Mols. $NaNO_3$ per 100 medium.	10^4k_1.
Series 1 :—Medium composition : H_2O, 67·8; HNO_3, 25·7; $HClO_4$, 6·5 mols. %.					
124	0·00	52·2	115	1·05	45·3
122	0·17	51·5	116	1·34	44·5
118	0·51	49·2	119	1·52	43·0
113	0·68	48·7	114	1·70	43·3
120	0·85	47·0	117	2·06	41·0
Series 2 :—Medium composition : H_2O, 72·4; HNO_3, 17·0; $HClO_4$, 10·6 mols. %.					
103	0·00	33·0	109	0·56	30·2
108	0·19	32·3	105	0·75	29·5
104	0·37	30·8	107	1·94	25·7
Series 3 :—Medium composition : H_2O, 72·6; HNO_3, 17·2; $HClO_4$, 10·2 mols. %.					
152	0·00	24·8	159	1·52	19·7
158	0·63	22·2	160	2·12	18·7
157	1·09	21·3			
Series 4 :—Medium composition : H_2O, 71·2; HNO_3, 21·8; $HClO_4$, 7·0 mols. %.					
139	0·00	9·88	141	1·31	8·95
150	0·24	9·72	147	1·48	9·03
143	0·32	9·73	140	1·64	8·73
146	0·49	9·62	148	1·97	8·68
144	0·66	9·38			
Series 5 :—Medium composition : H_2O, 75·6; HNO_3, 13·0; $HClO_4$, 11·4 mols. %.					
125	0·00	6·63	127	1·11	5·92
134	0·24	6·58	136	1·22	5·72
137	0·71	6·23	135	1·42	5·74
129	0·98	5·59	130	1·52	5·72

TABLE IV.

Effect of added sodium perchlorate on first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous solutions of nitric and perchloric acids.*

(Initially, $[C_6H_4{\cdot}SO_3Na] = 0{\cdot}169$M., throughout.)

Run No.	Mols. $NaClO_4$ per 100 of medium.	10^4k_1.	Run No.	Mols. $NaClO_4$ per 100 of medium.	10^4k_1.
Series 3 :—Medium composition as for Series 3 in Table III.					
152	0·00	24·8	156	0·84	34·3
154	0·32	28·0	155	1·06	39·3
153	0·57	31·5			

This effect of sodium perchlorate on the rate of nitration was directly confirmed by experiments such as those of the series recorded in Table IV. In this series, 2-phenylethylsulphonic acid was nitrated at 30·10° in solutions prepared by adding successively increasing amounts of sodium perchlorate to a medium of the same composition as was used for one of the groups of experiments on the effect of added sodium nitrate (Series 3 of Table III). Sodium perchlorate was thereby shown to have a marked accelerative effect on nitration in aqueous nitric and perchloric acids. This is illustrated by the uppermost curve in Fig. 9. A positive kinetic effect of salts on nitration in this type of medium is probably general for salts of very strong acids, since we have observed it again with sodium hydrogen sulphate as the added salt. (It is on this account that standard concentrations of sodium 2-phenylethylsulphonate or sodium benzylsulphonate were used in nearly all the present experiments.)

It need hardly be said that the kinetic behaviour of ionised salts in media already very concentrated with respect to ions cannot be treated on the basis of the theory of salt effects at low ionic strengths. A simple (and probably over-simplified) way of regarding the effect of non-reacting salts, such as sodium perchlorate, on nitration rates in aqueous nitric acid containing a strong acid, such as perchloric acid, is to suppose that the salt, presumably acting mainly through its cation, binds water, thereby making water less available for the binding of protons,

which accordingly combine to a greater extent with nitric acid, thus forming increased equilibrium concentrations of nitric acidium ion. The degrees of solvation which it is necessary to assume in order to account on this simple basis for the observed kinetic effects are not excessive. Thus, as one can find by measurements on the model represented by Fig. 8, the gradient of the sodium perchlorate curve shown in Fig. 9 would be given correctly if we should assume that each sodium perchlorate molecule leads to the binding of an average of about 0·8 molecule of water. Our picture of the nitration process does not require us to allow for any gross kinetic salt effect arising from the mechanism of the nitration itself. For the positive charge in the transition state of nitration pre-existed in the nitration medium as the charge on a hydroxonium ion; from which it was transferred, by way of nitric acid, to the aromatic ring, only to become the charge on a hydroxonium ion again at the end of the reaction. In short, the nitration process displaces ionic charges but does not create or destroy them.

(2.4) *Effect of Temperature on Nitration Rate.*—This has been cursorily investigated both for the nitration of 2-phenylethylsulphonic acid in aqueous solutions of nitric and perchloric acids, and for the nitration of benzylsulphonic acid in aqueous solutions of nitric and sulphuric acids, in each case over temperature ranges of only about 20°, no special attempt having been made to secure high accuracy in the measurement of the temperature coefficients. In the conditions used, the apparent energies of activation, E, in the equation $k_1 = Be^{-E/RT}$, lay within the interval 17—20 kcals. g.-mol.$^{-1}$, whilst the frequency factors, B, lay in the range $10^{9\cdot6}$ to $10^{12\cdot3}$ sec.$^{-1}$. An illustrative series of measurements is recorded in Table V.

TABLE V.

Effect of temperature on the first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of 2-phenylethylsulphonic acid in an aqueous solution of nitric and perchloric acids.

(Initially, $[C_6H_5 \cdot SO_3Na] = 0{\cdot}169$M. throughout.)

Medium: H_2O, 72·6; HNO_3, 17·2; $HClO_4$, 10·2 mols.%.

Run No.	Temp. (°K.).	10^4k_1 (obs.).	10^4k_1 (calc.).*	Run No.	Temp. (°K.).	10^4k_1 (obs.).	10^4k_1 (calc.).*
166	293·1	8·15	8·7	165	308·2	35·5	38·0
152	303·2	24·8	23·4	163	313·0	62·2	57·5

* Calculated from the equation $k_1 = 7{\cdot}5 \times 10^9 \times e^{-17,350/RT}$.

(3) *Experimental Methods.*

(3.1) *Materials.*—Sodium benzylsulphonate was prepared by the standard method from fractionated benzyl chloride and sodium sulphite. It was purified by crystallising it several times from ethyl alcohol (Found: C, 43·6; H, 4·2; S, 16·4; Na, 11·7. Calc.: C, 43·3; H, 3·6; S, 16·5; Na, 11·8%).

Sodium 2-phenylethylsulphonate was prepared from fractionated 2-phenylethyl alcohol, by conversion of the latter, with the aid of phosphorus tribromide, into 2-phenylethyl bromide, and treatment of the crude bromide, still containing some unconverted alcohol, with a solution of sodium sulphite (cf. Rupe, *Annalen*, 1913, **395**, 114; Evans, Mabbott, and Turner, *J.*, 1927, 1161). The salt was purified by alternately washing it with ethyl alcohol and crystallising it from water several times (Found: Na, 11·0, 11·05. Calc.: Na, 11·05%).

(3.2) *Dilatometric Methods.*—The tapless dilatometers of Benford and Ingold did not work well with the aqueous solutions involved in these experiments, owing to small, uncontrolled movements of the two meniscuses. On the other hand, these aqueous nitration media attacked the better kinds of tap-grease sufficiently slowly to permit the use of a tap. The dilatometers actually employed were similar in form to Benford and Ingold's dilatometer of "type C" (*J.*, 1938, 932), except that the bent capillary was supplied with a tap above the level of the bulb, and was made of wider bore than the straight capillary, in order to increase the speed with which the dilatometer could be filled. The tap, which was of the oblique-bore type with a blown key, was lubricated with Apiezon L grease. The level of the meniscus, which falls during the course of a nitration, was read with a cathetometer.

Nitration media were made up from sulphuric acid, or from aqueous perchloric acid, each purchased as pure, from nitric acid, free from nitrous acid, prepared as described in Part II (*J.*, 1950, 2400), and from water. When measurements of volume were involved, densities also were measured by the use of a density bottle, in order to permit the expression of compositions as mol.-fractions, or in any other desired form. The inorganic salts, sodium nitrate, ammonium nitrate, sodium hydrogen sulphate, and sodium perchlorate, all crystallised several times from water, and well-dried over phosphoric oxide, were added by weight to a known weight of salt-free medium.

The required weight of the sodium salt of the aromatic sulphonic acid was placed in a graduated flask, and there dissolved in the nitration medium by shaking at 0°. The solution was made up to the mark at 0°, and was then transferred to a bulb in which it was quickly cooled to about −25°, while the gas in the apparatus was pumped out for some minutes with a rotary oil pump. The object of this treatment was to avoid the subsequent formation of bubbles of gas in the dilatometer. A portion of the de-gassed solution was then brought more nearly to the temperature, usually between 20° and 40°, at which the kinetic run was to be conducted, and was transferred by suction into the dilatometer already immersed in the thermostat.

(3.3) *Analytical Control.*—An approximate method for the analytical control of completed dilatometric runs was devised. It involved diluting the solution from the dilatometer with water, reducing the nitro-compounds by the addition of zinc dust, diazotising the resulting amino-compounds, and developing an azo-colour with alkaline β-naphthol. A standard was provided by nitrating the sulphonic acid with aqueous nitric acid in the absence of perchloric or sulphuric acid. In this case the unconsumed nitric acid could be evaporated by hard pumping at a relatively low temperature, leaving the total product as a residue, which was shown by determination of its nitrogen content to be mononitrated (Found, for the nitration product of sodium 2-phenylethylsulphonate: N, 5·35. Calc., for a mixture of mononitro-derivatives: N, 5·53%).

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495. *Kinetics and Mechanism of Aromatic Nitration. Part IV. Nitration by Dinitrogen Pentoxide in Aprotic Solvents.*

By V. GOLD, E. D. HUGHES, C. K. INGOLD, and G. H. WILLIAMS.

The kinetics have been studied of the nitration of a number of halogen- and carbalkoxyl-substituted benzenes by dinitrogen pentoxide in aprotic solvents such as carbon tetrachloride. The kinetics are complicated; but analysis shows that there is a simple limiting kinetic form, which is distinguished as the uncatalysed reaction, and that upon this may be superposed small, medium, or large amounts of one or more of a family of reactions, all catalysed by nitric acid. On this account, the total reaction may be appreciably, or even strongly, autocatalysed by the formed nitric acid. The uncatalysed reaction can be approximately isolated; it is a second-order process obeying the rate law $v_0 \propto [ArH][N_2O_5]$. Its rate has a normal temperature coefficient. Its rate is increased in more polar solvents, but the effect is small. On the other hand, the reaction shows a large positive salt effect, ionic nitrates behaving in this respect no differently from salts of other anions (contrast results given in Parts II and III); but the salts appreciably disturb the kinetic form of the reaction. The catalysed reactions have lower temperature coefficients than the uncatalysed, and depend on higher powers of the nitric acid concentration than the first power. Consequently the catalysed reactions, including the autocatalytic effects, are made prominent by the use of low temperatures, and of high concentrations of initially introduced, or of formed, nitric acid. By using conditions which admit the catalysis only in a mild form, a single reaction of the catalytic family is developed. Its rate is proportional to the square of the nitric acid concentration, $v_3 \propto [ArH][N_2O_5][HNO_3]^2$. But the more strongly developed forms of catalysis and autocatalysis involve rates, or partial rates, depending at least on the cube of the nitric acid concentration, $v_3 \propto [ArH][N_2O_5][HNO_3]^3$, and probably on higher powers.

The uncatalysed reaction is interpreted as a nitrating attack on the aromatic molecule by the covalent dinitrogen pentoxide molecule. This agrees with the kinetic form of the reaction, with the absence of retardation by ionic nitrates, and with the small solvent effect on rate. Observations on products are consistent with the view that a reagent other than the nitronium ion is at work. The strong positive salt effect is attributed to the effect of ions in promoting the ionisation of dinitrogen pentoxide, and therefore in leading to more rapid nitration by nitronium ion, with disturbance to the kinetic form of the reaction.

The nitric-acid-catalysed reactions are interpreted as nitronium ion reactions, arising from the ionising action of nitric acid on dinitrogen pentoxide. The smallest number of nitric acid molecules which could be effective for ionising a molecule of dinitrogen pentoxide is considered to be 2; but higher numbers, 3 and 4 particularly, are likely to be utilised when available. Each ionised solvate produces a form of nitronium ion, and each contributes a nitrating reaction to the family of catalysed nitrations. The conclusion that the nitronium ion is at work is supported by the observation that the ratio in which chloronitrobenzenes are formed by the strongly catalysed (but not by the uncatalysed) nitration of chlorobenzene by dinitrogen pentoxide, is substantially the same as the ratio in which they are formed in the nitration of chlorobenzene by nitric acid.

(1) *Object and Background.*

(1.1) *Aim of this Work.*—The suggestions were made in Part I (Benford and Ingold, *J.*, 1938, 955) that a molecule $X{\cdot}NO_2$ will be capable of acting as a nitrating agent if X attracts electrons sufficiently strongly, and that the nitrating efficiency of such a molecule will largely be determined by the electron-attracting power of X. The most efficient nitrating agent arises when X attracts the shared electrons so strongly that it carries them away, so that one is left with the free nitronium ion. By covalently combining the nitronium ion with bases of successively increasing strength, a series may be constructed of real or possible nitrating agents, which should have progressively diminishing efficiencies, *e.g.*,

$$\overset{+}{N}O_2,\ H_2\overset{+}{O}{\cdot}NO_2,\ O_2N{\cdot}O{\cdot}NO_2,\ Ph{\cdot}CO{\cdot}O{\cdot}NO_2,\ HO{\cdot}NO_2.$$

In Part II (*J.*, 1950, 2400) nitration by the nitronium ion was established, and its mechanism was determined. In Part III (*J.*, 1950, 2441) an investigation directed to the study of nitration by the nitric acidium ion was described. It is interesting to see how far along the above series nitration can be realised; and therefore, in this paper, we describe a study of nitration by dinitrogen pentoxide. Nitration with the molecular form of this reagent is realised; but, as we shall find, the details are complicated owing to the great facility with which covalent dinitrogen pentoxide breaks down into its ions.

(1.2) *Previous Work on Nitration by Dinitrogen Pentoxide.*—Considering how often it has been suggested that the nitrating action of nitric acid, or that of mixtures of nitric and sulphuric acids, is due to dinitrogen pentoxide, the amount of exact information in the literature concerning the nitrating properties of dinitrogen pentoxide is remarkably slight. Lothar Meyer states (*Ber.*, 1889, **22**, 23) that Giersbach used it below 55° in the conversion of benzene into dinitrobenzene. Bamberger (*Ber.*, 1894, **27**, 584) and Hoff (*Annalen*, 1900, **311**, 92) studied the action of dinitrogen pentoxide on aromatic amines, which they found to be converted into *N*- and *C*-nitro-derivatives and a number of other products. Haines and Adkins record (*J. Amer. Chem. Soc.*, 1925, **47**, 1419) that benzene, toluene, and bromobenzene were very rapidly nitrated by dinitrogen pentoxide in carbon tetrachloride:

$$N_2O_5 + ArH = Ar{\cdot}NO_2 + HNO_3$$

but that nitrobenzene was not thus nitrated, although it was nitrated in a violent reaction with solid dinitrogen pentoxide. Spreckels (*Ber.*, 1919, **52**, 315) used a solution of dinitrogen pentoxide in carbon tetrachloride in order to effect a smooth mononitration of benzotrichloride, without hydrolytic loss of chlorine, for the purpose of a quantitative study of the orientation of nitration; and Cooper and Ingold (*J.*, 1927, 836) employed the same reagent, with the same object, in the example of the nitration of benzoyl chloride.

Klemenc and Schöller's investigation of nitration by dinitrogen pentoxide should be mentioned (*Z. anorg. Chem.*, 1924, **141**, 231), though, as regards the nitration mechanism which is involved, it is more closely connected with Part II than with this paper. They showed that a given amount of dinitrogen pentoxide, dissolved in sulphuric acid, acted like twice as many molecules of nitric acid, dissolved in the same solvent, with respect to the rate at which *m*-xylene-4 : 6-disulphonic acid is nitrated in such solutions. We now understand that this is because the solvent converts both solutes quantitatively into nitronium ion, two such ions being formed from each molecule of dinitrogen pentoxide, but only one from each molecule of nitric acid (cf. *J.*, 1950, papers nos. 499, 506, 508).

(2) *Qualitative Description of the Kinetics of Aromatic Nitration by Dinitrogen Pentoxide in Aprotic Solvents.*

(2.1) *Conditions and Methods of Kinetic Investigation.*—The kinetics of nitration of a number of benzene derivatives by means of dinitrogen pentoxide in various aprotic solvents have been studied, to a small extent by methods of chemical analysis, but mainly by the use of the dilatometer.

The high rates of nitration placed certain practical limitations on the aromatic compounds used, on the solvents, and on the temperatures. The following aromatic compounds were employed: Fluoro-, chloro-, and bromo-benzene; *o*-, *m*-, and *p*-dichlorobenzene; *p*-chlorobromobenzene; *p*-dibromobenzene; 1 : 2 : 4-trichlorobenzene; methyl, ethyl, and *tert.*-butyl benzoate; ethyl *p*-toluate; ethyl *m*-chlorobenzoate; ethyl phthalate. They all contain deactivating halogen or carbalkoxyl substituents, up to a maximum of three of the former or two of the latter. The relative deactivating effects of these substituents can be judged from the results of Bird, Ingold, and Smith's experiments by the competition method on the relative rates of nitration of certain monosubstituted benzenes (*J.*, 1938, 905, 918). In round figures, they found that a single fluorine or iodine substituent reduced nitration rate by a factor of about 6, a single chlorine or bromine substituent by a factor of about 30, and a single carbethoxyl group by a factor of about 300.

The following solvents were employed: Nitromethane, acetonitrile, chloroform, carbon tetrachloride. In addition, a series of mixtures of nitromethane and carbon tetrachloride were employed in the following proportions by volume: $MeNO_2 : CCl_4$ = 1 : 9, 3 : 7, 5 : 5, 7 : 3, 9 : 1. For brevity, these mixtures will be termed 1 : 9-NMCT, etc. Carbon tetrachloride was found to be the slowest of the pure solvents. The addition of 10% of nitromethane considerably improved the solubilities of some of the reactants, without increasing the reaction

rates unduly. A considerable proportion of the kinetic work was accordingly carried out either in carbon tetrachloride, or in the 1 : 9-NMCT mixture.

Temperatures were in the range −25° to +25°. The former limit is close to the freezing points of carbon tetrachloride and nitromethane, and is also near the lowest temperatures at which our thermostatic equipment would work with the high precision necessary for dilatometry.

For the determination of kinetic form, Ostwald's isolation method was always employed, either the aromatic compound or the dinitrogen pentoxide being kept in constant excess over the other reactant. Most of the runs were conducted with the aromatic compound in excess, so that the dependence of the rate on the concentration of dinitrogen pentoxide was under observation in each experiment. The dependence of the rate on the concentration of the aromatic compound was given, in the first place, by comparisons between different runs with different constant concentrations of aromatic compound. For some aromatic compounds the dependence of the rate on the concentration of aromatic compound was additionally determined by following runs in which the dinitrogen pentoxide was taken in constant excess.

(2.2) *General Kinetic Forms of Nitration.*—From the results of dilatometric runs made with the aromatic compound in excess, more than 500 reaction–time curves have been drawn. Amongst them, three broad classes can be recognised, *viz.*, (1) approximately exponential curves, (2) curves which run nearly linearly for much of their length, and (3) curves having pronounced sigmoid forms. Examples are shown in Figs. 1—3.

This classification might suggest that, when the aromatic compound is in constant concentration, we have a first-order reaction, a zeroth-order reaction, and an autocatalytic reaction, separately, or in superposition. However, a careful study of the curves shows that the whole series can be more simply and consistently regarded as a single family formed by the mixing of a non-catalysed first-order reaction with an autocatalytic reaction. Almost every gradation between the exponential and linear, and between the linear and sigmoid, forms is represented amongst the results, and none of the linear curves is more exactly linear than could correspond to superposed exponential and sigmoid forms.

This view is strengthened by consideration of the corresponding logarithmic plots, such as are illustrated in Figs. 4—6. The reactions which we have termed exponential give logarithmic plots which are accurately linear, not over the whole reaction, but only over a large proportion, say 80—90%, of it; and when an appreciable deviation from linearity does set in, its direction always corresponds to a reaction rate rising above the experimental rate in the latter part of the reaction. The nearly linear reactions give logarithmic plots to which just the same description applies, except that the deviation from linearity is larger, and sets in earlier, *e.g.*, after 50—70% of reaction. Finally, the sigmoid reactions give logarithmic plots which are again similar, except that the deviation is larger still, and sets in earlier still, *e.g.*, after 20—40% of reaction. Thus the exponential reaction appears as an approach to a limiting non-catalysed reaction, on which, in practice, small, moderate, or large amounts of the autocatalytic reaction are superposed.

The non-catalytic reaction is favoured relatively to the autocatalytic reaction by an increase of temperature, and by a reduction in the initial concentration of dinitrogen pentoxide. But there is no single, absolute requirement, either with respect to a minimum of temperature or to a maximum of dinitrogen pentoxide concentration; and one can often realise all the main kinetic types by changing only one of these variables, provided the other is not too extreme. The most nearly exponential reactions have been observed at temperatures above +10°, with initial concentrations of dinitrogen pentoxide below 0·1M.; but reactions of a more or less exponential kind have been found at temperatures as low as −10°, with dinitrogen pentoxide concentrations below 0·05M. Low temperatures, and high initial concentrations of dinitrogen pentoxide (the aromatic compound being still in constant excess), favour the autocatalytic reaction. No clear solvent effect on kinetic form has emerged, but most of the work has been done either in carbon tetrachloride or in 1 : 9-NMCT, and it is possible that these two solvents are too similar easily to reveal such an effect. The introduction, or the accidental inclusion along with the dinitrogen pentoxide, of a small amount of nitric acid greatly enhances the autocatalytic process [cf. Section (4.2)].

About 60 dilatometric runs have been carried out with dinitrogen pentoxide in constant excess, the time-variable concentration now being that of the aromatic compound. This study has been confined to the compounds, fluorobenzene, chlorobenzene, and *m*-dichlorobenzene, and to the single solvent, carbon tetrachloride. However, even within this more limited range of observation, a completely corresponding set of kinetic phenomena appear. We find reaction–time curves which are nearly exponential, others which for a large part of their length are

Figs. 1—6.

Illustrating kinetic types of aromatic nitration by dinitrogen pentoxide, the aromatic compound being in constant excess.

Fig. 1.

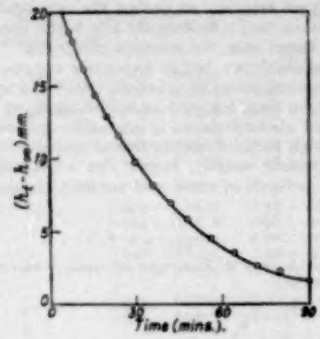


Fig. 2.

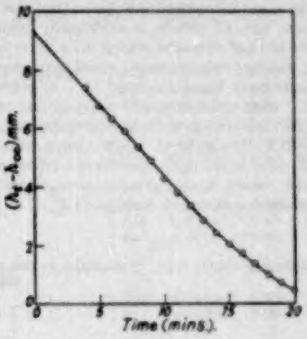


Fig. 3.

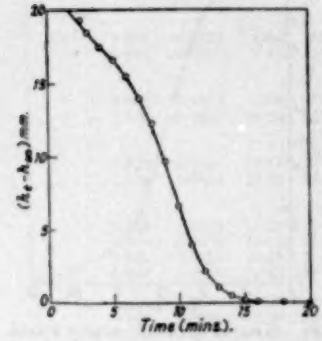


Fig. 4.

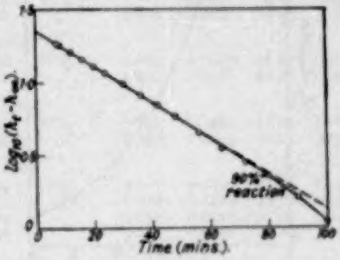


Fig. 5.

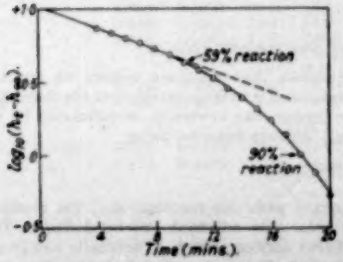
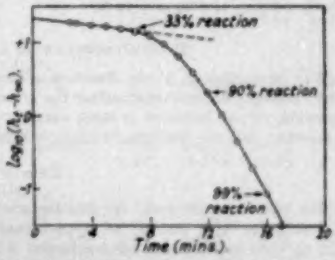


Fig. 6.



Figs. 1 and 4.—*" Exponential " reaction, illustrated by Run* 414. *Nitration of* p-$C_6H_4Cl_2$, *initially* 0·745*m.*, *by* N_2O_5, *initially* 0·0378*m.*, *in* CCl_4 *at* 14·99°.

Figs. 2 and 5.—*" Linear " reaction, illustrated by Run* 218. *Nitration of* C_6H_4Cl, *initially* 1·215*m.*, *by* N_2O_5, *initially* 0·0711*m.*, *in* CCl_4 *at* −10·00°.

Figs. 3 and 6.—*" Sigmoid " reaction, illustrated by Run* 447. *Nitration of* C_6H_4Cl, *initially* 1·037*m.*, *by* N_2O_5, *initially* 0·1212*m.*, *in* 1 : 9-NMCT *at* −9·77°.

nearly linear, and yet others which are markedly sigmoid. The exponential and sigmoid types are illustrated in Figs. 7 and 8. A careful study of all the curves shows that, as before, we are dealing with a limiting non-catalytic reaction, upon which varying amounts of an autocatalytic reaction are superposed.

The main circumstances favouring the non-catalysed reaction, as against the autocatalytic reaction, are, as before, a sufficiently high temperature, and a sufficiently low initial concentration of that reactant which is in deficit—in the present case, the aromatic compound. But again, neither requirement, considered separately, is absolute: rather accurately exponential reactions have been observed at −5° with initial concentrations of aromatic compound up to 0·05M.; and approximately exponential reactions have been followed at temperatures as low as −25°, although with considerably smaller initial concentrations of aromatic compound, *e.g.*, 0·01M. In general, a low temperature, and a high initial concentration of aromatic compound (the dinitrogen pentoxide remaining in constant excess), favour the autocatalytic reaction, which is also greatly strengthened if small amounts of nitric acid are introduced into the reaction system [cf. Section (4.2)].

FIG. 7. FIG. 8.

Illustrating kinetic types of nitration by dinitrogen pentoxide when the dinitrogen pentoxide is kept in constant excess.

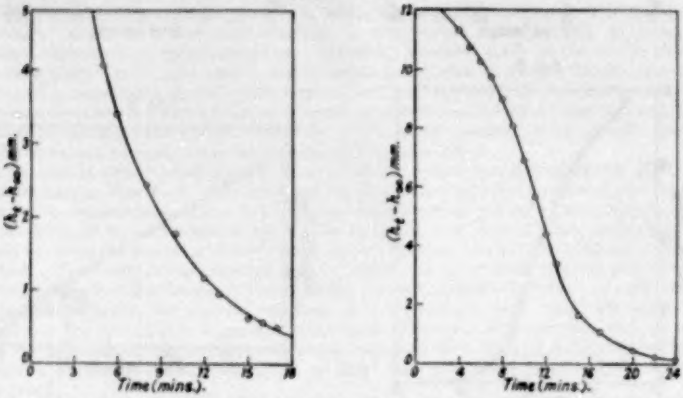


FIG. 7.—*"Exponential" reaction illustrated by Run* 685: *Nitration of* C_6H_5F, *initially* 0·011M., *by* N_2O_5, *initially* 0·402M., *in* CCl_4 *at* −24·55°.

FIG. 8.—*"Sigmoid" reaction, illustrated by Run* 684: *Nitration of* C_6H_5F, *initially* 0·030M., *by* N_2O_5, *initially* 0·402M., *in* CCl_4 *at* −24·55°.

(3) *Observations on the Limiting Non-catalytic Reaction.*

(3.1) *Molecularity of the Reaction.*—The observations that nitration follows an approximately exponential law when either the aromatic compound is in large excess over the dinitrogen pentoxide, or the latter is in large excess over the former, can evidently be correlated by the assumption that the limiting reaction is bimolecular, the rate equation being

$$\text{Rate} = k_2[\text{ArH}][\text{N}_2\text{O}_5]$$

This can be confirmed. From any one experiment with one reactant, say, the aromatic compound, in large excess, an approximate first-order rate constant can be derived. If a block of such experiments be conducted with different concentrations of aromatic compound (always in large excess over the dinitrogen pentoxide), all other conditions being the same, then the deduced first-order rate constants should be proportional to the concentrations of aromatic compound; and therefore, the second-order rate constants, obtained by dividing the first-order constants by the concentrations of aromatic compound, should not vary. How far this is true can be seen from Table I.

TABLE I.

First-order rate constants (k_1 *in sec.*$^{-1}$) *and second-order rate constants* (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *for exponential-type nitrations with dinitrogen pentoxide, the aromatic compound being in excess.*

No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.	No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.
Temperature 10·06°:											
				ArH = *p*-$C_6H_4Cl_2$.							
253	CCl_4	0·573	0·0514	1·82	3·18	260	1 : 9-NMCT	1·278	0·0405	8·52	6·67
255	,,	0·821	0·0514	2·51	3·06	266	,,	1·331	0·0552	8·50	6·39
257	1 : 9-NMCT	0·576	0·0466	4·63	8·04	265	,,	1·782	0·0552	10·31	5·79
256	,,	0·824	0·0466	5·94	7·21	262	3 : 7-NMCT	0·639	0·0385	9·57	14·98
267	,,	0·880	0·0552	6·40	7·27	263	,,	0·967	0·0385	11·97	12·38
261	,,	0·952	0·0405	7·14	7·50	264	,,	1·298	0·0385	13·96	10·75
Temperature 14·99°:											
272	CCl_4	0·696	0·0445	3·53	5·07	390	CCl_4	1·181	0·0610	6·29	5·33
389	,,	0·854	0·0610	4·51	5·28	400	,,	1·558	0·0424	8·60	5·52
403	,,	0·867	0·0424	4·97	5·74	388	,,	1·940	0·0610	10·29	5·30
273	,,	1·042	0·0391	5·65	5·42						
				ArH = *p*-C_6H_4ClBr.							
412	,,	0·535	0·0378	2·70	5·21	405	CCl_4	0·973	0·0424	5·70	5·86
411	,,	0·688	0·0378	3·75	5·45	404	,,	1·201	0·0424	6·38	5·31
				ArH = *p*-$C_6H_4Br_2$.							
413	,,	0·446	0·0378	2·36	5·29	414	CCl_4	0·745	0·0378	4·53	6·08
				ArH = *o*-$C_6H_4Cl_2$.							
420	,,	0·611	0·0427	5·04	8·25	423	CCl_4	1·106	0·0427	8·88	8·03
421	,,	0·880	0·0427	7·21	8·19	422	,,	1·420	0·0427	10·95	7·71
				ArH = *m*-$C_6H_4Cl_2$.							
418	,,	0·658	0·0669	8·20	12·46	415	CCl_4	1·069	0·0557	12·91	12·08
419	,,	0·889	0·0669	10·68	12·01	416	,,	1·342	0·0557	16·08	11·98
				ArH = C_6H_5·CO_2Me.							
429	,,	0·643	0·0434	10·61	16·34	431	CCl_4	1·211	0·0434	17·21	14·21
430	,,	0·833	0·0434	12·75	15·30	432	,,	1·499	0·0434	20·31	13·43
				ArH = C_6H_5·CO_2Et.							
192	,,	0·546	0·0410	10·21	18·70	196	CCl_4	0·871	0·0329	14·52	16·67
195	,,	0·578	0·0329	10·54	18·24	383	,,	1·076	0·0529	16·28	15·31
384	,,	0·692	0·0529	12·23	17·67	194	,,	1·093	0·0410	17·39	15·91
386	,,	0·802	0·0529	12·62	16·98	385	,,	1·354	0·0529	19·51	14·41
				ArH = C_6H_5·CO_2Bu^t.							
433	,,	0·566	0·0434	14·40	25·44	441	CCl_4	0·902	0·0571	19·98	22·15
439	,,	0·734	0·0571	17·44	23·76	440	,,	1·089	0·0571	22·10	20·67
				ArH = *p*-C_6H_4Me·CO_2Me.							
444	,,	0·556	0·0313	10·35	18·61	443	CCl_4	0·887	0·0571	16·02	18·06
198	,,	0·643	0·0329	11·97	18·61	445	,,	1·127	0·0313	17·76	15·76
442	,,	0·658	0·0571	13·07	19·86						
				ArH = *m*-C_6H_4Cl·CO_2Et.							
451	,,	0·616	0·0650	5·43	8·81	450	CCl_4	1·170	0·0650	9·71	8·30
446	,,	0·903	0·0437	7·77	8·60	452	,,	1·190	0·0650	10·38	8·72
				ArH = *p*-$C_6H_4Cl_2$.							
434	1 : 9-NMCT	0·627	0·0479	8·55	13·64	437	1 : 9-NMCT	0·998	0·0479	12·94	12·97
436	,,	0·813	0·0479	11·11	13·66	435	,,	1·285	0·0479	15·13	11·77
				ArH = 1 : 2 : 4-$C_6H_3Cl_3$.							
392	,,	0·533	0·0487	3·77	6·82	396	1 : 9-NMCT	0·912	0·0487	5·65	6·10
393	,,	0·696	0·0487	4·31	6·19	395	,,	1·056	0·0487	6·29	5·96
397	,,	0·796	0·0487	4·81	6·04	394	,,	1·201	0·0487	6·96	5·80
Temperatures 20·00°:											
				ArH = *p*-$C_6H_4Cl_2$.							
379	CCl_4	0·480	0·0443	4·94	10·29	382	CCl_4	1·080	0·0443	9·97	9·23
380	,,	0·680	0·0443	6·59	9·69	381	,,	1·785	0·0443	16·35	9·16
351	1 : 9-NMCT	0·501	0·0481	12·31	24·58	353	1 : 9-NMCT	1·026	0·0481	23·96	23·35
352	,,	0·633	0·0481	15·76	24·90						

TABLE I.—(*continued*).

No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.	No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.
Temperature 20·00°:											
				ArH = 1 : 2 : 4-$C_6H_3Cl_3$.							
343	,,	0·708	0·0486	9·74	12·34	340	1 : 9-NMCT	1·149	0·0431	11·44	9·96
342	,,	0·825	0·0431	9·14	10·67	368	,,	1·250	0·0342	12·98	10·04
				ArH = *o*-$C_6H_4(CO_2Et)_2$.							
346	,,	0·589	0·0586	9·26	14·02	349	1 : 9-NMCT	0·896	0·0481	12·45	13·90
347	,,	0·742	0·0486	10·61	14·30	350	,,	1·202	0·0481	15·74	13·09
				ArH = *p*-$C_6H_4Cl_2$.							
289	3 : 7-NMCT	0·708	0·0618	30·8	43·5	310	3 : 7-NMCT	0·785	0·1042	32·6	41·6
				ArH = 1 : 2 : 4-$C_6H_3Cl_3$.							
315	,,	0·569	0·0698	11·82	20·77	311	3 : 7-NMCT	1·168	0·0367	19·24	16·47
312	,,	0·775	0·0367	14·91	19·24	314	,,	1·190	0·0367	19·46	16·35
316	,,	0·869	0·0698	16·35	18·79						

It appears from the data that, as the initial concentration of aromatic compound is increased, the first-order rate constant always increases to a comparable extent, whilst the second-order constant either remains constant or changes (usually falls) only slightly; a fall of the order of 10%, while the concentration of aromatic compound is being increased 100%, is not uncommon. We should not expect exact constancy in the second-order constant for several reasons: the reactions, or most of them, are not quite kinetically pure; the excess of aromatic compound is not an infinite excess; and the proportion in which the aromatic compound is present is sufficient to render it an important constituent of the medium. It seems that the second-order constant shows a greater tendency to drop, with increasing concentration of the aromatic compound, when the nitrations are conducted in mixed nitromethane–carbon tetrachloride solvents than when they are carried out in pure carbon tetrachloride. As an example, the figures for the nitration of *p*-dichlorobenzene in 1 : 9-NMCT at 10° may be compared with those applying to the nitration of the same compound in carbon tetrachloride at 15°. The difference can be understood on the basis, which will be illustrated below, that nitromethane is a substantially faster solvent than carbon tetrachloride for these nitrations. Probably the aromatic halogen compounds belong to the class of somewhat slow solvents, and are much more nearly comparable, as solvents, to carbon tetrachloride than to nitromethane. Thus, in the presence of nitromethane, they will act as diluents towards the latter, diminishing its accelerative effect; and hence they will reduce bimoleuclar reaction rates much more than if the solvent were only carbon tetrachloride. Aromatic compounds which do not contain halogen, in particular, the alkyl benzoates and methyl *p*-toluate, appear to be even slower, as solvents, than carbon tetrachloride; for even in this solvent, as well as in the mixed solvents, their presence in considerable concentration reduces the bimolecular reaction rates. On the whole, then, the bimolecular nature of the limiting reaction seems confirmed by these comparisons.

(3.2) *Solvent Effect on the Bimolecular Reaction Rate.*—The effect of the solvent on the rates of the bimolecular reaction is illustrated by the second-order rate constants assembled in Table II. Owing to the effect of the aromatic compounds in acting as rate-reducing components of the more polar media, we ought to compare rate constants which have been extrapolated to zero concentration of the aromatic compound. This has been done for the halogen compounds, the necessary data being available. It could not be done for the two esters for lack of suitable data; and for these esters, therefore, the comparison of solvents has been made for finite, but fixed, concentrations of aromatic compound.

These figures show that polar solvents accelerate bimolecular nitration by dinitrogen pentoxide. But the acceleration is very moderate, a factor of the order of 6 apparently sufficing to cover the whole range from non-dipolar carbon tetrachloride to highly polar nitromethane. By way of contrast, the solvent effect on nitrations by nitric acid in organic solvents may be recalled (Part II, *J.*, 1950, 2400): alike for the zeroth-order and the first-order reactions, as observed in the presence of a constant excess of nitric acid, factors of the order of 40 separate the rates in acetic acid from those in nitromethane; and we would certainly expect very much larger factors between corresponding rates in carbon tetrachloride, if they could be measured, and the rates in nitromethane.

(3.3) *Salt Effects on Reaction Rate.*—Added salts, nitrates as well as other salts, have a strong accelerative effect on bimolecular nitration rates in NMCT solvents. This is illustrated in Table III.

TABLE II.

Effect of solvent on second-order rate constants (10^5k_2 *with* k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *of bimolecular nitration by dinitrogen pentoxide.*

ArH :	*p*-$C_6H_4Cl_2$.			*as*-$C_6H_3Cl_3$.	Ph·CO_2Et.	*o*-$C_6H_4(CO_2Et)_2$.
$[ArH]_0$:	zero	zero	zero	zero	0·8M.	0·8M.
Temp. :	10°	15°	20°	20°	20°	20°
Solvent.						
CCl_4	—	5·45	9·85	—	32 [1]	—
$CHCl_3$	—	—	—	—	44·1	—
1 : 9-NMCT	9·04	16·5	26·5	12·33	—	14·1
3 : 7-NMCT	18·5	—	—	24·73	—	—
5 : 5-NMCT	—	—	—	27·6 [2]	—	20·2
7 : 3-NMCT	—	—	—	—	—	22·7
9 : 1-NMCT	—	—	—	—	—	27·0
MeCN	—	—	—	—	—	29 [3]
$MeNO_2$	—	—	—	—	—	30·7

[1] Calculated as 1·7 times the value at 15°. [3] Extrapolation based on two runs only.
[2] Value at $[ArH]_0$ = 1·1M.

TABLE III.

Effect of added salts on second-order rate constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *of bimolecular nitration of* p*-dichlorobenzene in a nitromethane–carbon tetrachloride solvent.*

($[ArH]_0$ ~0·8M., $[N_2O_5]_0$ ~0·05M., Solvent 1 : 9-NMCT, throughout.)

No.	[Salt.]	10^4k_2.	No.	[Salt.]	10^4k_2.	No.	[Salt.]	10^4k_2.
(*Salt :* Tetraethylammonium picrate. *Temp. :* 10·03°.)			(*Salt :* Tetraethylammonium hydrogen sulphate. *Temp. :* 20·00°.)			(*Salt :* Tetraethylammonium nitrate. *Temp. :* 24·80°.)		
536	0	7·99	631	0	24·4	735	0	33·9
541	0·0018	12·51	633	0·00046	32·6	755	0·00045	37·5
539	0·0025	22·79	634	0·00093	38·7	756	0·00060	44·8
540	0·0040	30·56	637	0·0012	43·1			

Little can be said concerning the quantitative aspect of the effect, partly because one is limited to very small salt concentrations by the low solubilities of the salts, and partly because the salts appreciably disturb the kinetic form of the reaction, thereby divesting the rate constants of an exact significance. The disturbance can be described qualitatively by stating that the accelerative effect of a salt in any one experiment is less near the end of the run than near the beginning.

(3.4) *Effect of Added Nitric Acid on the Bimolecular Reaction Rate.*—Added nitric acid accelerates nitration by dinitrogen pentoxide. In some cases, particularly at the lower temperatures, the effect is very strong, and involves a pronounced change of kinetic form; for not only is there catalysis, but also the autocatalysis is notably increased. At higher temperatures, the whole accelerative effect is weaker, though it is still considerable; but the induced autocatalysis is much weaker, so that substantial increases of rate can be realised without serious complication to the kinetic form of the reaction. We illustrate this weaker and simpler type of effect in Table IV, for the nitration of *p*-dichlorobenzene in carbon tetrachloride at 20°; similar results have been obtained for the nitration of 1 : 2 : 4-trichlorobenzene in carbon tetrachloride at 25°.

TABLE IV.

Effect of added nitric acid on second-order rate constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *of bimolecular nitration of* p*-dichlorobenzene in carbon tetrachloride at* 20·03°.

($[ArH]_0$ ~0·6M., $[N_2O_5]_0$ ~0·04M., throughout.)

Run no.	$[HNO_3]_0$.	10^4k_2.	$11 + 80c^2$.	Run no.	$[HNO_3]_0$.	10^4k_2.	$11 + 80c^2$.
624	0	10·1	11·0	628	0·174	33·1	35·5
625	0·071	16·1	15·0	629	0·181	37·5	37·2
626	0·080	16·6	16·1	630	0·251	61·1	61·5

The experimental rate constants in Table IV agree fairly well with the requirements of the equation $10^4k_2 = 11 + 80c^2$, where $c = [HNO_3]_0$. The catalysed reaction is thus of approximately second order with respect to the nitric acid catalyst, over this range of conditions.

(3.5) *Effect of Temperature on the Bimolecular Reaction Rate.*—This has not been studied over a sufficient range of temperature, with any one aromatic compound and solvent, to allow

good Arrhenius parameters to be given. It can, however, be computed from the measured rates that the activation energies of the bimolecular reactions of *p*-dichlorobenzene in carbon tetrachloride and in 1 : 9-NMCT, and of 1 : 2 : 4-trichlorobenzene in the latter solvent, are close to 17 kcals., whilst the corresponding non-exponential factors of the Arrhenius equation have values in the neighbourhood of 10^{10} sec.$^{-1}$ g.-mol.$^{-1}$ l.

(3.6) *Effect of Aromatic Substituents on the Bimolecular Reaction Rate.*—Some rate constants for the bimolecular nitration by dinitrogen pentoxide of different aromatic compounds, in the same solvent at the same temperature, are collected in Table V. The values given have been extrapolated, where necessary, in order to eliminate the medium effect of the aromatic compound itself.

TABLE V.

Comparable second-order rate constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *for the bimolecular nitration of aromatic compounds by dinitrogen pentoxide.*

(Values correspond to $[ArH]_0 = 0$. Solvent CCl_4, temp. 15°, throughout.)

ArH.	10^4k_2.	ArH.	10^4k_2.	ArH.	10^4k_2.	ArH.	10^4k_2.
p-$C_6H_4Cl_2$	5·4	*o*-$C_6H_4Cl_2$	8·5	$C_6H_5{\cdot}CO_2Me$...	18·2	*p*-Me·$C_6H_4{\cdot}CO_2Me$	21·8
p-C_6H_4ClBr ...	5·5	*m*-$C_6H_4Cl_2$.....	12·1	$C_6H_5{\cdot}CO_2Et$ ...	21·7	*m*-Cl·$C_6H_4{\cdot}CO_2Et$	8·7
p-$C_6H_4Br_2$	5·7	1 : 2 : 4-$C_6H_3Cl_3$	2·5[1]	$C_6H_5{\cdot}CO_2Bu^t$	30·2	*o*-$C_6H_4(CO_2Et)_2$...	3·0[2]

[1] From observation in 1 : 9-NMCT at 15°, by division by 3·0 (cf. Table II). [2] From observation in 1 : 9-NMCT at 20°, allowing a factor 1·7 for the temperature difference (cf. Table I).

The only monosubstituted benzenes in the list are the benzoic esters. As to these, the illustrated accelerating effect of homology in the alkyl group is theoretically consistent with the known effect of homology in reducing the proportion in which *m*-nitration takes place (cf. Ingold, *Rec. Trav. chim.*, 1929, **48**, 801).

The figures for the di- and tri-substituted benzenes show that the methyl substituent is slightly activating, that the halogens deactivate moderately, chlorine and bromine behaving very similarly, and that carbalkoxyl groups deactivate more strongly. All this is qualitatively consistent with theory, and with the results derived for monosubstituted benzenes by the competition method (cf. Bird, Ingold, and Smith, *locc. cit.*); but the differences now obtained for the polysubstituted compounds are of distinctly smaller magnitude than those given by the competition method for the monosubstituted benzenes.

Of the three dichlorobenzenes, the *m*-compound is the least deactivated. This is intelligible, because halogens deactivate *m*-positions more strongly than they do *o*- and *p*-positions (*locc. cit.*); and *m*-dichlorobenzene is the only isomeride having positions available for substitution which are *not meta* with respect to any chlorine atom. Steric hindrance may exert a special effect in reducing the rate for *p*-dichlorobenzene, substitution in which is necessarily *ortho* with respect to one chlorine atom.

(4) *Observations on the Autocatalytic Reaction.*

(4.1) *Influence of Solvent, Temperature, and Concentration.*—It has not been found possible to represent the rates of the autocatalysed reactions by any single, chemically significant equation; and therefore our diagnostic material concerning this reaction consists essentially of its qualitative features, which, fortunately, are quite striking. Some features of the autocatalytic reaction have been described and illustrated already (Section 2.2); we shall here summarise them, and then add to them.

No major effect on the intensity of autocatalysis appears to result from a change of solvent from carbon tetrachloride to the mixed solvent 1 : 9-NMCT.

A reduction in the temperature of nitration has a notable effect in advancing the onset, and increasing the intensity, of autocatalytic acceleration, though a temperature lower than some fixed limit seems not to be a definite requirement for such acceleration if other conditions are favourable.

An increase in the concentration of whichever reactant is in deficit, whether it be the aromatic compound or the dinitrogen pentoxide—in other words, an increase in the concentration in which reaction products can be formed—leads to a similar advancement and intensification of the autocatalysis.

Nitric acid must be a product of nitration by dinitrogen pentoxide. It has been shown in Section 3.4 that the limiting bimolecular reaction is considerably accelerated by added nitric acid. Evidently the production of nitric acid by nitration might account for the autocatalysis.

(4.2) *Effect of Added Nitric Acid on the Autocatalysis.*—It has been observed that initially

added nitric acid not only accelerates nitration from the outset, but also increases the autocatalysis of the reaction. When the reaction observed in the absence of added nitric acid follows a course which is very close to that of the limiting bimolecular reaction, then the effect of added acid on the autocatalysis is not very noticeable. Advantage was taken of this for the purpose of studying the simple catalysis by nitric acid of the bimolecular reaction, as described in Section 2.4. However, the effect of added nitric acid on autocatalysis is very striking, when the reaction in the absence of nitric acid shows an appreciable (but still not large) departure from the strict bimolecular form—for instance, if it gives a reaction–time curve of shape intermediate between what we have termed the " exponential " and " linear " forms, one reactant being in constant excess. In such a case, added nitric acid may not only increase the rate from the commencement; it may also lead to the development of an actual acceleration during an intermediate period of the run, so that the reaction–time curve now assumes a sigmoid form.

This effect is illustrated in Fig. 9, in which two reaction–time curves are shown. The runs represented by these curves were strictly comparable as to initial conditions, except that a small amount of nitric acid was added to one of them. The slower of the two is the control, the rate of which drops continuously as reaction proceeds. The other reaction (the one affected by the added nitric acid) is not only generally faster, but also exhibits a rising rate during a considerable part of its course.

FIG. 9.
Effect of added nitric acid.

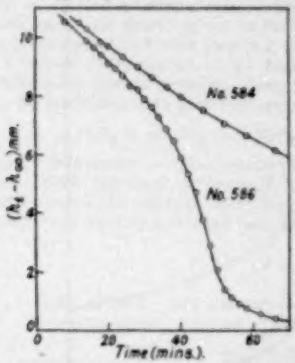


FIG. 10.
Effect of added sulphuric acid.

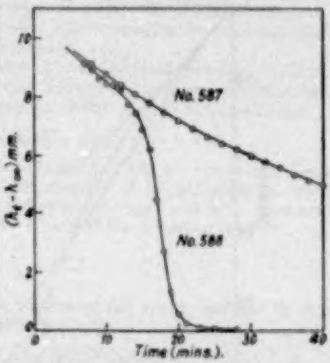


FIG. 9.—*Nitration of* C_6H_5Cl, *initially* 1·375M., *by* N_2O_5, *initially* 0·049M., *in* CCl_4 *at* −10·35°. *Run* 584. *No initial* HNO_3. *Run* 586. *Initially added* HNO_3 = 0·021M.

FIG. 10.—*Nitration of* C_6H_5Cl, *initially* 1·375M., *by* N_2O_5, *initially* 0·045M., *in* CCl_4 *at* −10·35°. *Run* 587. *No initial* H_2SO_4. *Run* 588. *Initially added* H_2SO_4 = 0·0019M.

Assuming the autocatalysis to be due to formed nitric acid, these results mean that, the higher the instantaneous concentration of nitric acid, the more sensitive is the rate to a given increment of produced nitric acid. In other words, the dependence of the rate on nitric acid must involve a higher power of concentration than the first. Even a second-power dependence is found to be insufficient to account for the magnitude of some of the effects observed (cf. Section 5).

(4.3) *Effect of Added Sulphuric Acid on the Autocatalysis.*—Qualitatively similar results have been obtained by the initial addition of sulphuric acid. Again the strongest effects on the autocatalysis arise in nitrations which, in the absence of added acid, show an appreciable (but still only a small) departure from the limiting bimolecular form. Sulphuric acid is more potent than nitric acid for the intensification of the autocatalysis.

An illustration is given in Fig. 10. Again the reaction in which no sulphuric acid is added initially, that represented by the upper curve, becomes progressively slower throughout its course (only part of which is shown in the diagram), whilst a reaction carried out under identical conditions, except that a small amount of sulphuric acid was added initially, develops, as the lower curve illustrates, a powerful autocatalytic acceleration.

Since the action of sulphuric acid on an excess of dinitrogen pentoxide must obviously give rise to nitric acid, the effects of the two acids in promoting the autocatalysis of nitration by dinitrogen pentoxide are evidently closely connected.

(5) *Discussion of the Mechanisms of Nitration.*

(5.1) *A Mathematical Model illustrating the Kinetic Forms of Nitration.*—Consider the consequences of supposing that the rate of nitration, v, of ArH by N_2O_5 is expressed by the equation

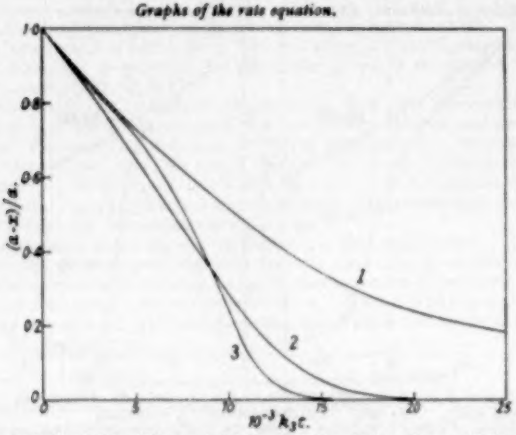
$$v = k_2(a - x) + k_3(a - x)(b + x)^3$$

where a = initial $[N_2O_5]$, if ArH is in constant excess, or
= initial [ArH], if N_2O_5 is in constant excess,
b = initial $[HNO_3]$, and
x = formed $[HNO_3]$ = formed $[ArNO_2]$.

This equation assumes the total reaction to be the sum of an uncatalysed part and a catalysed part. The uncatalysed reaction has been shown (Section 2.2 and 3.1) to be bimolecular: accordingly its rate must be of first-order form, as the equation represents it, if, in accordance with the conditions of our measurements, one reactant is taken to be in constant excess. The

FIG. 11.

Graphs of the rate equation.



(1): $a = 0{\cdot}04$, $b = 0{\cdot}00$, $k = 0{\cdot}04$. (2): $a = 0{\cdot}04$, $b = 0{\cdot}04$, $k = 0{\cdot}04$. (3): $a = 0{\cdot}10$, $b = 0{\cdot}00$, $k = 0{\cdot}04$.

catalysed reaction is assumed to be of the same molecularity with respect to the reactants, and therefore, under the conditions of the measurements, to be of the first order with respect to either reactant. The catalysed reaction is assumed to depend also on the third power of the concentration of nitric acid. We shall not now attempt to justify the use of the third power in the present illustration; but it will be suggested in Section 5.2 that this power lies within the range of a series of powers which are thought to be in general simultaneously operative.

The integrated form of the equation is

$$k_3t = \frac{1}{(a+b)^3 + h^3} \cdot \ln\frac{a}{a-x} + \frac{1}{3h^3(a+b+h)} \cdot \ln\frac{h+b+x}{h+b} +$$

$$\frac{2h - (a+b)}{6h^3\{(a+b)^2 - h(a+b) + h^2\}} \cdot \ln\frac{(x+b)^2 - h(x+b) + h^2}{b^2 - hb + h^2} +$$

$$\frac{(a+b)}{\sqrt{3}h^3\{(a+b)^2 - h(a+b) + h^2\}} \cdot \left\{\tan^{-1}\frac{2(x+b) - h}{\sqrt{3}h} - \tan^{-1}\frac{2b - h}{\sqrt{3}h}\right\}$$

where $k = (k_4/k_3)^{1/3}$. Some graphs of this equation are shown in Fig. 11. It is immediately apparent that graphs 1, 2, and 3 are qualitatively similar to the experimental curves shown in Figs. 1, 2, and 3, and in some of the other figures in this paper. In particular, we find that, when a is low and b is zero, curves are obtained, which may be of approximately exponential form, and in any case represent a velocity continuously diminishing with time (graph 1). When a is higher, and b is still zero, curves of greater slope are obtained, which may run nearly linearly for a large part of their length. When a is higher still, with b still zero, the curves assume a sigmoid form, representing an autocatalytic acceleration at some time after the commencement of reaction (graph 3). We observe a similar series of changes when, starting again from the case in which a is low and b is zero, a is kept constant and b is given a succession of increasing finite values: the curves again pass through a nearly linear form (graph 2), and finally become sigmoid.

Evidently two of the factors which have been found to control the incidence of autocatalytic acceleration are directly reproduced in this model, *viz.*, the intensification of autocatalysis on increasing the initial concentration of whichever reactant is in deficit, and its intensification by the initial introduction of nitric acid. As to the third factor, *viz.*, temperature, we may, quite generally, expect the fourth-order reaction to be less important at higher temperatures, as it would have a lower entropy and energy of activation than the first-order reaction.

We have investigated the effect of assuming catalysis by nitric acid according to other powers of its concentration than the third. The assumption of a first-power, or of a second-power, catalysis leads to curves which show some flattening relatively to the non-catalytic curve, but which do not assume a markedly sigmoid form. On the other hand, as one might expect, the use of the fourth power of the nitric acid concentration produces sigmoid curves which are more sharply inflected than that illustrated.

(5.2) *Chemical Interpretation of the Kinetics of the Catalysed Reaction.*—Let us introduce the hypothesis, at first in a general form, that nitric acid catalyses nitration by dinitrogen pentoxide by combining with it to form aggregates, which may be of various sizes:

$$N_2O_5 + nHNO_3 \rightleftharpoons N_2O_5,nHNO_3, \text{ where } n = 1, 2, 3, \ldots$$

This equation is intended to indicate only the composition, and not the chemical nature, of the aggregates. Each aggregate is assumed to be capable of participating in nitration. For conditions in which one reactant, let us say, the aromatic compound, is in constant excess, the expression for the reaction rate must take such a form as the following, *viz.*,

$$v = \sum_{n=0}^{n} k_n[X_n]$$

where $X_n = N_2O_5,nHNO_3$. The uncatalysed portion of the rate is included through the term in $n = 0$. Assuming rapidly attained equilibria, we have

$$[X_n] = K_n[N_2O_5][HNO_3]^n$$

the K_n being equilibrium constants; and therefore the rate equation can be written

$$v = \Sigma k_n K_n (a - x)(b + x)^n$$

Here $K_0 = 1$, and k_0 has values which can readily be determined by experiment. The higher K_n must diminish as n increases beyond a certain point, because the size of the aggregates must be limited for steric and dynamical reasons. We shall show presently that k_n should be expected to increase with n over a certain range. Hence it may well be that, under our conditions, the term $n = 0$, and some intermediate term, such as $n = 3$, for which k_nK_n is maximal, will represent the two most important parts of the rate.

This generalised hypothesis evidently interprets, at least as well as the simplified model did, the main kinetic features of nitric acid catalysis, especially the factors which determine the incidence and intensity of autocatalytic acceleration. The effect of temperature may be described more specifically than before: the aggregates will be formed exothermically; and hence, as the temperature is raised, they will be reduced in size, and the larger ones in number; and thus sensitivity to catalysis by nitric acid will be reduced at higher temperatures.

Let us now consider the nature of the aggregates more particularly. We know that dinitrogen pentoxide dissolved in organic solvents, such as carbon tetrachloride and nitromethane, consists entirely of covalent molecules. We also know that, when dissolved in nitric acid, dinitrogen pentoxide consists entirely of nitronium and nitrate ions, which are strongly and exothermically solvated by nitric acid (Ingold and Millen, *J.*, 1950, paper no. 510; Gillespie, Hughes, and Ingold,

ibid., paper no. 504). Therefore we must expect that, when small amounts of nitric acid are added to a solution of dinitrogen pentoxide in some aprotic solvent, the nitric acid molecules will concentrate towards each molecule of dinitrogen pentoxide, and, when present in sufficient amount to solvate ions and thus to liberate energy, will bring about ionisation of the dinitrogen pentoxide, and perhaps dissociation of the ions.

The smallest number of nitric acid molecules that can readily be pictured as effective for the ionisation of a molecule of dinitrogen pentoxide is 2, *i.e.*, one molecule to take care of each ion. Thus it is reasonable to suppose that the limit of weak catalysis by nitric acid might be represented by the term $n = 2$. The weak catalysis observed at higher temperatures does in fact operate according to a quadratic law, as has been illustrated in Section 3.4.

The solvation number of dinitrogen pentoxide dissolved in pure nitric acid has been found to be 4, two nitric acid molecules being combined with each of the two ions (Gillespie, Hughes, and Ingold, *loc. cit.*). This solvation number is likely to depend in part on the exothermicity of transfer of a nitric acid molecule from the nitric acid medium to the ions. The exothermicity of a transfer of nitric acid from a largely aprotic medium to the ions might well be greater. Hence the conclusion is, not that $n = 4$ necessarily represents a maximum for aggregate formation from an ample supply of nitric acid, but that n can rise at least as high as 4 in aprotic solvents under suitable conditions. Thus we believe that the kinetic terms corresponding to $n = 2$, 3, and 4 at least can be effective, though which of them will be dominating will depend on the circumstances.

The ionic dissociation is doubtless endothermic, and hence we must expect that increased exothermic solvation of the ions by nitric acid will increase the dissociation. Thus the larger the value of n, the more will the nitronium ion behave like a " free " ion, *i.e.*, one liberated from the influence of a neutralising anion. This is the basis of our view (cf. Section 1.1) that the rate constant k_n of nitration by X_n will increase with n over the range of effective values of n.

To summarise, we find that all the main kinetic features of the catalysis by nitric acid, and of the autocatalysis, of nitration by dinitrogen pentoxide can be interpreted on the basis that the nitric acid molecule exerts its catalytic effect by aggregating around the originally covalent dinitrogen pentoxide molecules, thereby causing ionisation and ionic dissociation. The nitrating entity in the catalysed nitration is thus the nitronium ion, which is progressively freed by the solvating nitric acid from the influence of anions. Nitration by the nitronium ion involves, as was shown in Part II (*J.*, 1950, 2400), the slow addition of the nitronium ion to the aromatic molecule, with the formation of a complex cation, which rapidly ejects a proton. In the present case, the proton must eventually combine with a nitrate ion. The steps may be formulated as follows:

$$NO_2{\cdot}O{\cdot}NO_2 + (x+y)HNO_3 \overset{\text{fast}}{\rightleftharpoons} \overset{+}{N}O_2(xHNO_3) + \overset{-}{N}O_3(yHNO_3)$$

$$ArH + \overset{+}{N}O_2(xHNO_3) \xrightarrow{\text{slow}} \overset{+}{Ar}H(NO_2) + xHNO_3$$

$$\overset{+}{Ar}H(NO_2) \xrightarrow{\text{fast}} ArNO_2 + \overset{+}{H}$$

$$\overset{+}{H} + \overset{-}{N}O_3(yHNO_3) \xrightarrow{\text{fast}} (y+1)HNO_3$$

Catalysis by sulphuric acid is attributed to the direct formation of nitronium ions, and, simultaneously, of nitric acid molecules; and, in minor degree, to the replacement of nitrate ions by the less nucleophilic hydrogen sulphate ions.

(5.3) *Nature of the Nitrating Agent in the Uncatalysed Reaction.*—The above analysis of the mechanism of the catalysed reaction involves the conclusion that the nitrating entity in the uncatalysed reaction is the covalent dinitrogen pentoxide molecule. Several independent indications confirm this conclusion.

Suppose that we did not accept it. Then we might try to account for the kinetic order of the uncatalysed reaction on the basis that, in aprotic solvents, there is a rapidly attained equilibrium between covalent dinitrogen pentoxide and its ions, and that the nitronium ion, in small stationary concentration, effects the nitration. Any such equilibrium proportion of nitronium ions, and of nitrate ions, would have to be assumed to be very small, since in fact it is beyond the limits of detection by ordinary physical means. It follows that the rate of the uncatalysed reaction must be very strongly depressed by small amounts of added nitrate ions (cf. Part II, *J.*, 1950, 2400). This is not according to the evidence: it was shown in Section 3.3 that tetraethylammonium nitrate (like tetraethylammonium picrate and the hydrogen sulphate) accelerates the uncatalysed reaction.

The further point arises that, with all three salts, the acceleration is very large, the amount

of salt needed to double the reaction rate in 1 : 9-NMCT being in each case of the order of M/1000. We explain this effect as a kind of catalysis, which depends, like catalysis by nitric acid, on the great ease with which covalent dinitrogen pentoxide molecules will split into ions in a suitable environment. We assume that, in this case, ionisation of the dinitrogen pentoxide is promoted by association with the ions of the added salt. That pre-formed ions do promote the ionisation of dinitrogen pentoxide molecules is suggested by the circumstance that each such molecule splits into ions as it adds itself to the ionic lattice of a crystal of dinitrogen pentoxide (Ingold, Millen, and Poole, *Nature*, 1946, **158**, 480; Millen, *J.*, 1950, paper no. 509), which is growing, either in the vapour, or in a solution containing, as solute, only the molecular form of the substance.

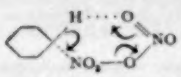
Again, the solvent effect on the bimolecular reaction rate indicates that this reaction occurs between the aromatic compound and the non-ionised dinitrogen pentoxide molecule. It was shown in Section 3.2 that polar solvents increase nitration rate, but do so only slightly, a factor of the order of 6 covering the whole range of investigated solvents from carbon tetrachloride to nitromethane. Since the initial materials are indubitably neutral molecules, this small solvent effect makes it certain that the products formed immediately on completion of the rate-determining stage are neutral molecules, and not ions. Therefore the entity which attacks the aromatic molecule must be the dinitrogen pentoxide molecule, and not the nitronium ion. The observed small solvent effect is consistent with the idea of a transition state which, though neutral as a whole, is dipolar, and because of its polarity is somewhat more solvated than are the original reactants.

Summarising, we conclude that the uncatalysed nitration of aromatic compounds by dinitrogen pentoxide in aprotic solvents is a single-stage bimolecular process, involving direct attack by the non-ionised dinitrogen pentoxide molecule :

$$ArH + NO_2{\cdot}O{\cdot}NO_2 \longrightarrow ArNO_2 + HNO_3$$

Speculatively, one may suggest a cyclic form (inset) for the transition complex.

One other point may be mentioned, even though it has yet been studied only in a preliminary way. It has been noticed that the proportions in which mononitro-isomerides are formed in the nitration of an aromatic compound by the nitric-acid-catalysed reaction of dinitrogen pentoxide, and by the non-catalysed reaction of this nitrating agent, are in some cases very different. Thus, in the catalysed nitration of chlorobenzene by dinitrogen pentoxide, the proportion in which *p*-chloronitrobenzene is formed is practically the same as that in which Holleman found this isomeride in the product of the nitration of chlorobenzene by nitric acid; whereas, in the non-catalysed nitration of chlorobenzene by dinitrogen pentoxide, the proportion of formed *p*-chloronitrobenzene is distinctly smaller. This is consistent with our conclusion that different nitrating agents are operative in the two types of nitration. It is satisfactory that the orientational data for the catalysed nitration agree with data for nitration in nitric acid; for it is certain that in this medium the nitrating entity is the nitronium ion (Part II, *J.*, 1950, 2400).



(6) *Experimental Methods.*

(6.1) *Materials.*—The required aromatic compounds, organic solvents, and tetraethylammonium salts were prepared or purified by standard methods. The mixed NMCT-solvents were prepared by making 99·96 c.c. of nitromethane up to 1000·0 c.c. at 20·0° with carbon tetrachloride, 29·94 and 49·98 c.c. of nitromethane each up to 100·0 c.c. at 20·0° with carbon tetrachloride, and 29·70 and 9·97 c.c. of carbon tetrachloride each up to 100·0 c.c. at 20·0° with nitromethane. Nitric acid was purified as described in Part II.

Dinitrogen pentoxide was prepared in all-glass apparatus by the dehydration of nitric acid with phosphoric oxide, followed by sublimation on to phosphoric oxide, and resublimation, in a stream of ozonised oxygen. The method and apparatus were similar in principle to those of Russ and Pokorny (*Monatsh.*, 1913, **34**, 1053), Daniels and Bright (*J. Amer. Chem. Soc.*, 1920, **42**, 1133), and Chédin (*Ann. Chim.*, 1937, **8**, 243), but the passage of ozone, along with dinitrogen pentoxide vapour, through drying tubes of commercial phosphoric anhydride, which largely decomposes the ozone (Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 1852), was avoided. A stiff paste of nitric acid and phosphoric oxide, prepared at −30°, was gradually warmed to 33° during the first sublimation in ozonised oxygen, while the dinitrogen pentoxide was collected at −80°. Ground glass joints were sealed with phosphoric acid, except that the joint of the tube in which the product was collected was kept dry. At each end of the gas-train, traps of sulphuric acid and phosphoric oxide excluded moisture, while heated sections of tube prevented the egress of ozone. Prepared samples * of dinitrogen pentoxide were preserved in the dark at −80°.

* They were crystalline and colourless. We did not obtain dinitrogen pentoxide in the form of a yellow liquid at −40°, as recently described by Angus *et al.* (*Nature*, 1949, **184**, 433).

(6.2) *Dilatometric Methods.*—These were essentially the methods of Benford and Ingold (*J.*, 1938, 929) with the improvements mentioned by Hughes, Ingold, and Reed (*J.*, 1950, 2400). Benford and Ingold's tapless dilatometers of "type C" were employed. Solutions of the aromatic compound, and of the dinitrogen pentoxide, were allowed 8 minutes to approach the temperature of the thermostat, before being mixed and drawn into the dilatometer. The pre-mixing period was standardised, because of the thermal (unimolecular) decomposition of dinitrogen pentoxide: standardisation ensures that, in all experiments carried out at the same temperature, the same small fraction of dinitrogen pentoxide will have decomposed before the beginning of the timed run. The zero of time was taken as the time of mixing. Nitration by dinitrogen pentoxide is accompanied by a contraction. But for 3—7 minutes after mixing, no significant readings could be obtained owing to thermal disturbances.

Graphical methods have been used for evaluating the results. For the investigation of kinetic form, either the variable part of the dilatometric height ($h_t - h_\infty$), or its logarithm, was plotted against the time (t). As mentioned in Section 2.1, reactions of an essentially bimolecular nature were brought to an approximately first-order kinetic form by the use of a large excess of one reactant. For the determination of first-order constants, Guggenheim's method of plotting from paired readings was followed. The derived rate-constants are, in principle, the sums of the rate-constants of all the first-order processes occurring in the dilatometer, *viz.*, the nitration, and the thermal decomposition of dinitrogen pentoxide. In order to isolate the rate constant corresponding to nitration, we should subtract from the over-all first-order constant the rate constant for the decomposition of dinitrogen pentoxide. This correction is just appreciable near the upper end of our range of temperatures, and, when significant, it was always applied. The rate constants for the decomposition of dinitrogen pentoxide were taken from data by Eyring and Daniels (*J. Amer. Chem. Soc.*, 1930, **52**, 1472), values for mixed solvents being computed by interpolation.

(6.2) *Chemical Control of the Dilatometric Runs.*—The methods by which a check was kept on what was being measured in the dilatometric runs were in general as described in Part II (*J.*, 1950, 2400). For present illustration, we shall refer to chemical examinations made of the products of a few completed runs, and then give an example of a run followed chemically throughout.

The product from a dilatometric run of first-order type on *p*-dichlorobenzene, in carbon tetrachloride, with the aromatic compound in excess over the dinitrogen pentoxide, was washed with water, and dried; and the solvent was then evaporated below room temperature under reduced pressure. The nitro-compounds were reduced by means of tin and hydrochloric acid, the tin was removed by hydrogen sulphide, and, after the latter had been boiled off, the solution was made alkaline. The amines were extracted with ether, distilled completely, and analysed (Found: C, 44·9; H, 3·2; N, 8·0; Cl, 43·6. Calc. for $C_6H_5Cl_2{\cdot}NH_2$: C, 44·5; H, 3·1; N, 8·6; Cl, 43·7%).

The product from a dilatometric run of autocatalytic type on chlorobenzene in 1 : 9-NMCT, with the chlorobenzene in excess over the dinitrogen pentoxide, was evaporated below room temperature under reduced pressure, in order to remove the solvent, the nitric acid, and the excess of chlorobenzene. The residual yellow solid was analysed (Found: C, 44·8; H, 2·7; N, 8·6; Cl, 22·5. Calc. for $C_6H_4Cl{\cdot}NO_2$: C, 45·7; H, 2·6; N, 8·9; Cl, 22·5%).

The product of a dilatometric run on chlorobenzene in carbon tetrachloride, with the dinitrogen pentoxide in excess over the chlorobenzene, was worked up in a similar way, and the yellow solid residue was analysed (Found: C, 46·0; H, 2·6; N, 8·8; Cl, 22·0%). This experiment shows that the use of a large excess of dinitrogen pentoxide does not lead to dinitration.

When a run was to be followed throughout by chemical analysis, it was conducted in an all-glass system consisting of a bulb furnished with a narrow delivery tube leading to an automatic pipette. The bulb was immersed in the thermostat, whilst the delivery tube and pipette had jackets through which the thermostat liquid was driven by means of a circulating pump. Samples (6 c.c.) were withdrawn into the pipette by suitable adjustments of the pressure in the apparatus, which was protected at both ends from the incursion of moisture. The samples were delivered into portions of 100 c.c. of acetone, to which 1% of water had been added, in order to secure hydrolysis of unchanged dinitrogen pentoxide. The acid then present was titrated with aqueous sodium hydroxide, lacmoid being the indicator. The end-points were good at first; but they deteriorated as the run proceeded, probably on account of the formation of small amounts of nitrophenolic by-products, which form coloured salts with alkalis. An example of this type of experiment is recorded in Table VI.

TABLE VI.

Illustrating the kinetics of nitration by dinitrogen pentoxide as followed by chemical analysis.

Nitration of *p*-dichlorobenzene by dinitrogen pentoxide in carbon tetrachloride at 14·99°. Initially $[C_6H_4Cl_2] = 0{\cdot}599$M., and $[N_2O_5] = 0{\cdot}0488$M. Samples of 6·0 c.c. titrated with 0·0435N-sodium hydroxide. First-order rate constants, k_1, in sec.$^{-1}$.

Time (sec.).	Titre (c.c.).	10^4k_1.	Time (sec.).	Titre (c.c.).	10^4k_1.
0	13·56	—	2512	11·01	2·79
109	13·37	3·59	3458	10·16	3·28
774	12·76	2·23	5870	9·55	2·74
1404	11·92	2·84	∞	8·55	—

Mean rate constant: $k_1 = 2{\cdot}9 \times 10^{-4}$ sec.$^{-1}$.

A dilatometric experiment under very nearly the same conditions gave the value $k_1 = 3{\cdot}0 \times 10^{-4}$ sec.$^{-1}$.

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496. *Kinetics and Mechanism of Aromatic Nitration. Part V. Nitration by Acyl Nitrates, particularly by Benzoyl Nitrate.*

By V. Gold, E. D. Hughes, and C. K. Ingold.

The nitration of benzene by benzoyl nitrate in carbon tetrachloride has been kinetically examined. With the benzene in constant excess, the reaction was approximately of first order. The rate was found to vary with the sample of benzoyl nitrate. Preparations of benzoyl nitrate always contain benzoic anhydride. It was shown that added benzoic anhydride depressed the rate of nitration of benzene by a given sample of benzoyl nitrate. This suggested that benzoyl nitrate might be exerting its nitrating action through a small stationary concentration of dinitrogen pentoxide, formed, along with benzoic anhydride, in the rapidly established equilibrium,

$$2BzO\cdot NO_2 \rightleftharpoons N_2O_5 + Bz_2O.$$

Confirmation was secured by examining the effect of benzoic anhydride on the nitrating properties of dinitrogen pentoxide. The latter in carbon tetrachloride nitrated benzene instantly under the conditions of this work. But the addition of excess of commercial benzoic anhydride at once reduced the nitrating power of the dinitrogen pentoxide to approximate equivalence with that of benzoyl nitrate. Commercial benzoic anhydride contains benzoic acid. Pure benzoic anhydride did not act on dinitrogen pentoxide in carbon tetrachloride in the way described; but it did so, if some benzoic acid also was introduced. Thus, a rapid establishment of the above-written equilibrium requires the presence of acid.

Consistently, it was shown that, with a fixed concentration of benzoic acid, the rate of nitration of benzene by dinitrogen pentoxide and excess of benzoic anhydride was decreased by increasing the excess of the latter; and that, with fixed concentrations of benzoic anhydride, the rate of nitration was decreased by increasing the concentration of benzoic acid. From this it is concluded that the above anhydride–anhydride equilibrium, catalysed by acid, arises by combination (addition) of the two anhydride–acid equilibria,

$$N_2O_5 + BzOH \rightleftharpoons BzNO_3 + HNO_3$$
$$Bz_2O + HNO_3 \rightleftharpoons BzNO_3 + BzOH$$

No evidence could be secured that benzoyl nitrate directly attacks the aromatic molecule: its nitrating action seems to be exerted entirely through dinitrogen pentoxide. Experiments by Cohen and Wibaut make a like conclusion probable for the acetyl nitrate, presumed to be present in solutions of nitric acid in excess of acetic anhydride.

(1) *Objects and Background.*

(1.1) *Related Work on the Kinetics of Nitration.*—In Part I (*J.*, 1938, 929) the principles were mentioned by which one might set down a series of actual or possible nitrating agents in the theoretically expected order of diminishing reactivity, *e.g.*,

$$NO_2^+,\ NO_2\cdot OH_2^+,\ NO_2\cdot O\cdot NO_2,\ NO_2\cdot OBz,\ NO_2\cdot OH.$$

In Parts II, III, and IV (preceding papers), this series has been examined to the following extent: nitration by the nitronium ion has been established; the nitric acidium ion has been shown to dissociate into, and nitrate through, the nitronium ion, but nitration also by the nitric acidium ion itself has been made plausible; and again, the dinitrogen pentoxide molecule has been shown to dissociate into, and nitrate through, the nitronium ion, although nitration also by the undissociated molecule has been realised.

These studies led to a consideration of the fourth member of the above series, in principle a mixed anhydride of nitric acid and a weaker acid, the example being benzoyl nitrate. Expecting this to be a nitrating agent of low efficiency, one might have expected even greater difficulty than before in suppressing nitration through more active nitrating agents formed by its decomposition, and hence greater difficulty in establishing nitration by the original undecomposed molecule. This has been our experience. The decompositions of benzoyl nitrate to more active nitrating agents are on the whole more prominent, and more complicated, than are those of the nitrating agents treated in the preceding studies. Because of this, the nature of the decomposition through which benzoyl nitrate acts as a nitrating agent has been established only in a qualitative way. It is not possible to assert, as a result of the present work, that benzoyl nitrate cannot directly engage in nitration, but no evidence of any such behaviour has been found.

Referring to the last member of the series of nitrating agents written above, we may recall that nitration by nitric acid proceeds, as far as is known (cf. Parts I—III), entirely through either the nitronium ion or the nitric acidium ion. No evidence has been encountered that the

nitric acid molecule *per se* can directly engage in nitration. This paper therefore completes the present phase of our study of the above series by the method of reaction kinetics.

(1.2) *Previous Work on Nitration by Acyl Nitrates.*—Lachowicz observed (*Ber.*, 1884, **17**, 1281) that, when benzoyl chloride is heated with silver nitrate, benzoic anhydride is formed together with oxides of nitrogen. Francis reinvestigated this reaction at lower temperatures with a view to isolating intermediates (*J.*, 1906, **89**, 1; *Ber.*, 1906, **39**, 3798). He obtained a yellow oil, which he regarded as benzoyl nitrate, formed in the first of the following series of reactions, which proceed further at higher temperatures:

$$BzCl + AgNO_3 = BzNO_3 + AgCl$$
$$2BzNO_3 = Bz_2O + N_2O_5$$
$$2N_2O_5 = 2N_2O_4 + O_2$$

The analytical data for the yellow oil did not agree with the formula of benzoyl nitrate, but it was suggested that this was due to the presence of benzoic anhydride—a plausible interpretation in view of the ready decomposition of the oil, the known production of benzoic anhydride, and the volatility of oxides of nitrogen.

Francis showed that his benzoyl nitrate could be used to nitrate aromatic compounds in aprotic solvents such as carbon tetrachloride. He investigated particularly benzenoid hydrocarbons and phenol derivatives. Further work on hydrocarbons has been reported by Willstätter and Kubli (*Ber.*, 1909, **42**, 4151), and on phenols and phenol ethers by Oxford (*J.*, 1926, 2004) and by Griffiths, Walkey, and Watson (*J.*, 1934, 631). The last-named investigators made the important observation that the ratio *ortho*/*para* in which isomerides are formed in the mononitration of anisole by benzoyl nitrate is much higher than that in which they are produced in nitration either by mixed nitric and sulphuric acids, or by nitric acid alone, or by nitric acid in acetic acid, *i.e.*, by reagents which are now known (cf. Part II) to react through the nitronium ion.

The use, for aromatic nitration, of solutions of nitric acid in excess of acetic anhydride was introduced by Orton (*J.*, 1902, **81**, 806). Pictet and Khotinsky reported the isolation of acetyl nitrate from solutions of dinitrogen pentoxide in acetic anhydride (*Compt. rend.*, 1907, **144**, 210; *Ber.*, 1907, **40**, 1163). Its nitrating properties resembled those of Orton's solutions, and also those of Francis's benzoyl nitrate. It gave high *ortho*/*para* ratios for the nitration of several monosubstituted benzenes. This has been confirmed in a quantitative investigation by Holleman, Hartogs, and van der Linden (*Ber.*, 1911, **44**, 717) on the nitration of acetanilide with Orton's mixture, and in one by Griffiths, Walkey, and Watson (*loc. cit.*) on the nitration of anisole with this reagent, which they found to behave quite similarly to benzoyl nitrate, and very differently from the group of reagents now recognised as reacting through the nitronium ion.

In the present observations on the kinetics of nitration, we have used benzoyl nitrate, rather than acetyl nitrate, because of the tendency of the latter to explode during isolation. Reference will be made later (Section 3.2) to the kinetic study, reported by Cohen and Wibaut (*Rec. Trav. chim.*, 1935, **54**, 409), of nitration with Orton's mixture.

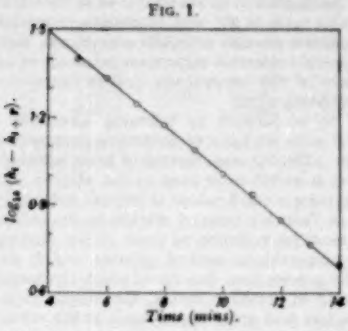
(2) *Kinetic Observations.*

(2.1) *Nitration by Benzoyl Nitrate.*—As heretofore, the dilatometric method of following the kinetics of nitration was adopted. Chemical analysis was employed as a check. Carbon tetrachloride was used as solvent throughout the work. It was found that benzene could be nitrated, at temperatures near 20°, by means of benzoyl nitrate in carbon tetrachloride at rates convenient for dilatometric observation; and accordingly, benzene was taken as the substance to be nitrated in most of the experiments of the present series.

A number of samples of benzoyl nitrate were prepared by Francis's method. Kinetic experiments on the nitration of benzene in constant excess with this reagent in carbon tetrachloride at 20° indicated a reaction of approximately first order with respect to the nitrating agent. This is illustrated by the linearity of the logarithmic plot in Fig. 1. However, the first-order rate constants varied from run to run, as is illustrated in Table I, in a manner which suggested that some impurity, present in different proportions in the different samples of benzoyl nitrate, was affecting the rate of nitration. Since the work of Lachowicz and of Francis shows that benzoic anhydride is a decomposition product of benzoyl nitrate, and is normally present in preparations of the latter, the effect on nitration rate of added benzoic anhydride was tested. Table II shows the results obtained in a pair of runs, which were made with the same sample of benzoyl nitrate, all conditions being the same, except that, in one of

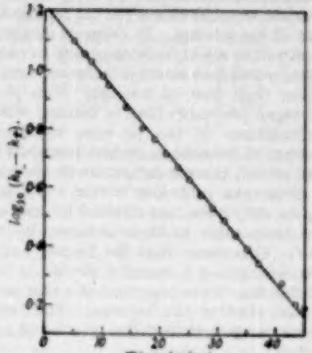
the runs, some benzoic anhydride was introduced. These and similar experiments established that added benzoic anhydride depresses the rate of nitration of benzene by benzoyl nitrate.

FIG. 1.



Nitration of benzene in constant excess by benzoyl nitrate, prepared by Francis's method, in carbon tetrachloride at 20°. Kinetics illustrated by Run No. 16. Plot covers 85% of reaction.

FIG. 2.



Nitration of benzene in constant excess by a mixture of dinitrogen pentoxide, benzoic anhydride, and benzoic acid, in carbon tetrachloride at 20°. Run No. 150. Plot covers 90% of reaction.

TABLE I.

Some first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of benzene in excess by benzoyl nitrate in carbon tetrachloride at 19·90°.

(Initially, $[C_6H_6] = 4{\cdot}47$M.; $[BzNO_3] = 0{\cdot}030$M.)

Run No.	8	10	11	14	15	16
10^4k_1	29·1	39·4	38·4	32·0	28·4	30·3

TABLE II.

Illustrating the effect of benzoic anhydride on the first-order rate constant (k_1 in sec.$^{-1}$) of nitration of benzene in excess by benzoyl nitrate in carbon tetrachloride at 20·00°.

(Initially, $[C_6H_6] = 2{\cdot}36$M.; $[BzNO_3] = 0{\cdot}030$M.)

Run No.	Added $[Bz_2O]$.	10^4k_1.	Run No.	Added $[Bz_2O]$.	10^4k_1.
251	—	44·0	252	0·035	20·0

These results suggested that benzoyl nitrate might be exerting its property of nitration through a small stationary concentration of the presumably more reactive entity, dinitrogen pentoxide, formed, along with benzoic anhydride, in the following rapidly reversible process:

$$2BzO{\cdot}NO_2 \rightleftharpoons Bz_2O + N_2O_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Accordingly the series of experiments next to be described was directed towards the building-up of a nitrating agent equivalent to benzoyl nitrate from the components benzoic anhydride and dinitrogen pentoxide.

(2.2) *Nitration by Mixtures of Dinitrogen Pentoxide, Benzoic Anhydride, and Benzoic Acid.*—The above hypothesis of the nitrating action of benzoyl nitrate requires the following statements to be true under the experimental conditions: (*a*) dinitrogen pentoxide must be an intrinsically more active nitrating agent than benzoyl nitrate; (*b*) the equilibrium between the three anhydrides must lie towards the left in the reaction as written above, *i.e.*, an excess of benzoic anhydride, added to dinitrogen pentoxide, must destroy nearly the whole of the latter; and (*c*) the rate at which this reaction proceeds to equilibrium must be greater than the rate at which the aromatic compound is nitrated.

Condition (*a*) is satisfied. This becomes obvious when we compare the kinetic runs reported in this paper with those in the preceding paper. Most of the runs with benzoyl nitrate as the nitrating agent have been carried out with benzene as the substance nitrated, the solvent being carbon tetrachloride, and the temperature 20°. But benzene is nitrated by dinitrogen pentoxide in carbon tetrachloride much too rapidly to allow the kinetics to be followed even at the freezing-point of the solvent. In order to obtain measurable rates at 20° with dinitrogen pentoxide as the nitrating agent, it is necessary to employ much less reactive aromatic compounds, such as *p*-dichlorobenzene or ethyl benzoate, which have specific nitration rates some hundreds of times smaller than that of benzene. This is a measure of the intrinsically greater reactivity of dinitrogen pentoxide than of benzoyl nitrate as nitrating agent.

Conditions (*b*) and (*c*) were together shown to be fulfilled by following kinetically the nitration of benzene in carbon tetrachloride at 20° with mixtures of dinitrogen pentoxide and (commercial) benzoic anhydride as nitrating agent. The benzene, instead of being nitrated by the dinitrogen pentoxide within a few seconds, as it would have been in the absence of the benzoic anhydride, was nitrated by mixtures containing a small excess of benzoic anhydride at rates comparable to those obtained by the use of Francis's benzoyl nitrate as the nitrating agent. This shows that the benzoic anhydride must have destroyed most of the dinitrogen pentoxide, giving a material similar in nitrating properties to benzoyl nitrate; and it shows that this must have happened at a rate considerably greater than the rate at which the resulting material nitrated the benzene. The benzene being in constant excess, the kinetic form of these runs again indicated a reaction of approximately first order with respect to the nitrating agent.

In these experiments, which were intended to be of a preliminary nature, the dinitrogen pentoxide was carefully prepared according to our usual routine; but the benzoic anhydride was the commercial material, and it contained free benzoic acid. When the runs were repeated with our own benzoic anhydride, which was free from benzoic acid, different results were obtained. The benzoic anhydride did not now depress initial rates of nitration by dinitrogen pentoxide, and, in particular, did not reduce the rate of nitration of benzene to a measurable order of magnitude. Indeed, the dinitrogen pentoxide even began to nitrate the benzoic anhydride, much as it would have nitrated a benzoic ester, had one been present, according to the experiments described in the preceding paper.

The runs were therefore again repeated, but with the addition of benzoic acid, as well as of pure benzoic anhydride. The nitrating power of the dinitrogen pentoxide was once more greatly reduced by the added substances. In the presence of a reactive aromatic compound, such as benzene, very little nitration either of benzoic acid or of benzoic anhydride took place. Instead, the benzene was nitrated at rates comparable to those which had been obtained either with benzoyl nitrate as the nitrating agent, or by the use of mixtures of dinitrogen pentoxide with commercial benzoic anhydride. Again, with the benzene in constant excess, the kinetics indicated a reaction of approximately first order with respect to the nitrating agent, as is illustrated by the logarithmic plot in Fig. 2.

TABLE III.

Effect of benzoic anhydride on the first-order rate constant (k_1 *in sec.*$^{-1}$) *of nitration of benzene in excess by dinitrogen pentoxide in carbon tetrachloride at* 20·00° *in the presence of a fixed amount of benzoic acid.*

(Initially, $[C_6H_6] = 2{\cdot}36$M.; $[BzOH] = 0{\cdot}0633$M.)

Run No.	Initial $[N_2O_5]$.	Initial $[Bz_2O]$.	10^4k_1.	Run No.	Initial $[N_2O_5]$.	Initial $[Bz_2O]$.	10^4k_1.
145	0·0305	0·0346	21·1	150	0·0265	0·1025	9·12
153	0·0341	0·0417	14·0	156	0·0341	0·1435	9·35
148	0·0214	0·0696	10·23	152	0·0265	0·1721	7·30
154	0·0341	0·0753	12·45	151	0·0265	0·2050	6·15
155	0·0341	0·0753	12·20				

Experiments were carried out in order to ascertain the effect of the addition of different initial amounts of benzoic anhydride, and of benzoic acid, on the rate of nitration of benzene by dinitrogen pentoxide. The results of one such series of experiments are reported in Table III. Here the concentrations of benzene and of benzoic acid were kept constant, and that of the dinitrogen pentoxide was given certain fixed values, whilst the concentration of the benzoic anhydride was varied from run to run. Some sets of runs of a different kind are reported in Table IV. In these, the concentrations of benzene and benzoic anhydride were fixed, whilst the concentrations of dinitrogen pentoxide and of benzoic acid were varied.

TABLE IV.

Effect of benzoic acid on the first-order rate constants (k_1 *in sec.*$^{-1}$) *of nitration of benzene in excess by dinitrogen pentoxide in carbon tetrachloride at 20·00° in the presence of fixed amounts of benzoic anhydride.*

(Initially, $[C_6H_6] = 2{\cdot}36$M.)

Run No.	Initial $[N_2O_5]$.	Initial $[Bz_2O]$.	Initial [BzOH].	10^4k_1.	Run No.	Initial $[N_2O_5]$.	Initial $[Bz_2O]$.	Initial [BzOH].	10^4k_1.
145	0·0305	0·0346	0·0633	21·1	158	0·0354	0·1025	0·0282	18·05
146	0·0242	,,	0·1267	10·7	150	0·0265	,,	0·0633	9·12
149	0·0265	0·0696	0·0254	18·6	157	0·0354	,,	0·1267	7·74
148	0·0214	,,	0·0633	10·65					

The figures in Tables III and IV are not suitable for quantitative treatment, because some of the initial concentrations have no simple significance for the whole kinetic runs, to which the quoted rate constants apply. However, it is obvious from Table III that, with fixed concentrations of benzene and of benzoic acid, the rate of nitration diminishes with increasing concentration of benzoic anhydride. It can be shown by means of a graphical representation of the figures that, for a fixed initial concentration of dinitrogen pentoxide, the reciprocal of the first-order rate constant increases approximately linearly with increasing concentration of benzoic anhydride. It also appears that, for a fixed concentration of benzoic anhydride, the rate constant increases with the initial concentration of dinitrogen pentoxide. All this is true for a fixed concentration of benzoic acid. The figures in Table IV show that, for fixed concentrations of benzene and benzoic anhydride, the rate of nitration diminishes with increasing concentration of benzoic acid.

(3) *Discussion.*

(3.1) *Mechanisms of Nitration by Benzoyl Nitrate.*—It has been shown in Section 2 that the rate of nitration of benzene by benzoyl nitrate, prepared by Francis's method, is depressed by added benzoic anhydride. It has also been shown that rates of nitration by benzoyl nitrate can be simulated by employing, as the nitrating agent, mixtures of dinitrogen pentoxide and benzoic anhydride, provided that they contain some free benzoic acid. Finally, it has been established that the first-order rate constants for the nitration of benzene in constant excess by mixtures of dinitrogen pentoxide, benzoic anhydride, and benzoic acid, increase with the concentration of dinitrogen pentoxide, when the concentrations of benzoic anhydride and of benzoic acid are constant, and decrease with increasing concentration of either benzoic anhydride or benzoic acid when the other concentrations are fixed.

Nearly all these effects are qualitatively interpreted by the hypothesis that benzoyl nitrate exerts its nitrating power through the nitrating action of a small concentration of dinitrogen pentoxide, which is formed along with benzoic anhydride in the reversible reaction (1) (p. 2469). It appears that this reaction attains equilibrium only slowly in the absence of acids, but that it runs rapidly to equilibrium under the catalytic influence of benzoic acid, which is usually present in the systems now considered, unless special measures are taken to secure its exclusion.

The observation which this hypothesis does not cover is the decrease of rate of nitration, by fixed concentrations of dinitrogen pentoxide and benzoic anhydride, in the presence of increasing concentrations of benzoic acid. In order to accommodate this finding, we assume that, in addition to the anhydride–anhydride equilibrium (1), an anhydride–acid equilibrium is set up, one form of which is shown in equation (2):

$$N_2O_5 + BzOH \rightleftharpoons BzNO_3 + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Assuming equilibrium, it makes no difference whether we regard the benzoic acid as directly destroying dinitrogen pentoxide as represented in equation (2), or as acting analogously on benzoyl nitrate, as in equation (3), thereby producing benzoic anhydride, which destroys dinitrogen pentoxide according to equation (1). Thus the alternative form (3) of the anhydride–acid equilibrium,

$$BzO{\cdot}NO_2 + BzOH \rightleftharpoons Bz_2O + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is not independent of (2). In other words, the equilibrium conditions for the reactions (1), (2), and (3) are expressible in terms of only two equilibrium constants. Reactions (2) and (3) evidently provide a mechanism for reaction (1), accommodating its acid catalysis. It follows that the presence of benzoic acid will always involve the presence of nitric acid; and that the catalysis of reaction (1), which we have described as catalysis by benzoic acid, must not be

regarded as specific to that acid. Such reactions should be subject to a general catalysis by acids.

On the whole, the case for assuming that benzoyl nitrate nitrates by way of dinitrogen pentoxide seems as strong as qualitative evidence can make it.* The preceding paper shows that the dinitrogen pentoxide may nitrate directly, although in some circumstances it will act through the nitronium ion.

(3.2) *Mechanism of Nitration by Acetyl Nitrate and by Solutions of Nitric Acid in Acetic Anhydride.*—No kinetic study has yet been made of aromatic nitration as effected by isolated acetyl nitrate. However, as was noted in Section 1.2, there is a good deal of evidence indicating that the nitrating properties of solutions of nitric acid in acetic anhydride are due to the formation of acetyl nitrate; and Cohen and Wibaut have recorded a study of the kinetics of the nitration of benzene by means of such solutions (*loc. cit.*).

According to our conclusions concerning the mode of nitration by benzoyl nitrate, we should expect nitration by acetyl nitrate, or by a solution of nitric acid in acetic anhydride, to proceed by way of dinitrogen pentoxide, formed in the following system of balanced reactions:

$$HNO_3 + Ac_2O \rightleftharpoons AcOH + AcNO_3$$
$$HNO_3 + AcNO_3 \rightleftharpoons AcOH + N_2O_5$$

and therefore,

$$2AcNO_3 \rightleftharpoons Ac_2O + N_2O_5$$

Cohen and Wibaut's kinetic results for the nitration of benzene by solutions of nitric acid in an acetic anhydride solvent are, as the authors point out, very difficult to interpret, because of the simultaneous occurrence of nitration of the acetic anhydride. Indeed, the conditions for their main series of experiments seem to have been somewhat unhappily chosen. However, the authors have also provided a limited body of data concerning the nitration of benzene by nitric acid, in the presence of acetic anhydride, under conditions in which the disturbance of side-reactions is much less serious, *i.e.*, in carbon tetrachloride as solvent, with the addition of only small amounts of acetic anhydride. The recorded results indicate, as is concluded by the authors, that the rate of nitration is increased by decreasing the concentration of acetic anhydride. The authors interpret this as a solvent effect; but if it should be simply a solvent effect on nitration by nitric acid, or by some entity formed from nitric acid without the direct participation of acetic anhydride, then still greater rates should be obtained if the latter substance is omitted altogether. Apparently Cohen and Wibaut did not test this inference; but we have tested it, although in doing so we had to add a little nitromethane to the carbon tetrachloride solvent, because nitric acid, in the absence of any acetic anhydride, is only slightly soluble in pure carbon tetrachloride. We find that nitric acid, when dissolved in this mixed carbon tetrachloride solvent, at concentrations of the order of those used by Cohen and Wibaut, does not nitrate benzene at 20° to any detectable extent. When a small quantity of acetic anhydride is added, nitration supervenes; but there is an optimum amount of this reagent, and an excess of it tends to suppress nitration.

The parallelism between these observations and those relating to the effect of added benzoic anhydride on rate of nitration by benzoyl nitrate is evident. We may reasonably infer, first, that the nitrating power of solutions of nitric acid in acetic anhydride is indeed due to the formation of acetyl nitrate, and secondly, that the nitrate acts by a mechanism similar to that which we have already derived for nitration by benzoyl nitrate, *i.e.*, by way of dinitrogen pentoxide, reversibly formed in the system of equilibria written above.

(4) *Experimental Methods.*

(4.1) *Preparation of Materials.*—Benzoyl nitrate was prepared by Francis's method in an all-glass apparatus. The benzoyl chloride was introduced into the reaction bulb by distillation, together with enough carbon tetrachloride to reduce its freezing point below −15°. The silver nitrate, previously fused, ground, and dried in a vacuum over phosphoric oxide, was added by rotating a side-tube attached by a lubricated ground-glass joint. A vent, through phosphoric oxide, allowed gaseous products, which were formed in only small amount, to pass out of the reaction chamber. After the conclusion of the reaction, which was conducted with continuous stirring below −15°, the solution was passed through a

* Even with the simplest assumptions, *viz.*, that mixtures of dinitrogen pentoxide, benzoyl nitrate, benzoic anhydride, nitric acid, and benzoic acid, always preserve equilibrium, and that nitration by such mixtures proceeds through molecular dinitrogen pentoxide only, the hypothesis offered in the text leads to an expression for the nitration rate which is algebraically complicated, and involves three disposable constants. For this reason, we have not attempted its quantitative experimental confirmation.

ground-glass filter by inverting the apparatus; and thus the mixture of benzoyl nitrate and carbon tetrachloride was collected. It was stored at about −10°, and diluted for use, as required, with dry carbon tetrachloride.

Benzoic anhydride was prepared as usual from benzoic acid and excess of acetic anhydride. After a preliminary purification by distillation under diminished pressure, the product was washed in ethereal solution with aqueous sodium hydroxide in order to remove all free benzoic acid; and the ether was then dried by means of calcium chloride and a little potassium carbonate, and distilled. The benzoic anhydride thus obtained was finally purified by crystallisation from light petroleum.

Dinitrogen pentoxide was prepared as described in the preceding paper.

(4.2) *Dilatometric Methods.*—The apparatus and method for following the kinetics of nitration by dilatometry were substantially as described in the preceding paper. For the nitrations by benzoyl nitrate, a fixed volume of the stock solution of benzoyl nitrate in carbon tetrachloride was delivered from a pipette into additional carbon tetrachloride, and, after 10 minutes allowed for the mixture to attain the temperature of the thermostat, the benzene, also at thermostat temperature, was added from a pipette, and the dilatometer, already immersed in the thermostat, was filled with the mixture. For the study of the effect of benzoic anhydride on nitration by benzoyl nitrate, the same procedure was used, except that the sample from stock of benzoyl nitrate dissolved in carbon tetrachloride was delivered into a solution of benzoic anhydride in carbon tetrachloride. In the experiments with dinitrogen pentoxide, a measured volume of a solution of this substance in carbon tetrachloride was added to a solution of benzoic anhydride, or of benzoic anhydride and benzoic acid, in carbon tetrachloride, and the whole was allowed 8 minutes to attain the temperature of the thermostat, before the benzene was added and the dilatometer filled.

The course of two dilatometric runs is shown graphically in Figs. 1 and 2 (p. 2469).

(4.3) *Analytical Control.*—Analytical checks on the dilatometric measurements were carried out exactly as described in the preceding paper, and the results were generally similar. Rate constants obtained by following the change of acidity agreed approximately with corresponding rate constants determined dilatometrically, the latter being the more precise.

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497. *Cryoscopic Measurements in Sulphuric Acid. Part I. Principles and Methods. The Cryoscopic Constant and Some Other Constants of Sulphuric Acid.*

By R. J. GILLESPIE, E. D. HUGHES, and C. K. INGOLD.

The experimental methods of cryoscopy in solvent sulphuric acid have been developed to a degree of precision sufficient for the evaluation of electrochemical equilibrium constants. The theoretical principles underlying a thermodynamically correct expression of the results are considered; and, van't Hoff's i-factors having led to confusions of concept which it seems impossible now to resolve, ν-factors are introduced, and are defined as a function only of numbers of solute particles, effects of forces being left for description by means of activity coefficients.

The methods and principles having been established, their first application was in a determination of the cryoscopic constant of sulphuric acid. This has not been satisfactorily measured hitherto, partly because the techniques were not accurate, and partly because substances were believed to dissolve without ionisation, which in fact are ionised in solution. We have found only two substances which dissolve freely in sulphuric acid without any apparent reaction, *viz.*, sulphuryl chloride and chlorosulphonic acid. Their use provides the first of three cryoscopic methods by which the required constant has been determined. The second method uses ionised sulphates, and the third employs certain organic oxygen-compounds which behave as infinitely strong bases. For most solvents, such a use of such solutes would be excluded by electrostatic non-ideality; but the dielectric properties of sulphuric acid are so extreme that, in certain concentration ranges, these solutes can be employed.

Revised values are given for the cryoscopic constant, for the heat of fusion, and for the melting point of sulphuric acid.

(1) *Principles and Methods.*

(1.1) *Aim of this Work.*—The experiments to be reported in this series of papers were originally undertaken with the object of elucidating by cryoscopic measurements certain ionogenic reactions in sulphuric acid, which had come to notice during kinetic studies on the mechanism of aromatic nitration. The formation of the nitronium ion from nitric acid in sulphuric acid was first clearly demonstrated by means of measurements of the depression of the freezing point of sulphuric acid by dissolved nitric acid (*Nature*, 1946, **158**, 480). However,

the aim of the cryoscopic studies soon expanded beyond its originally contemplated limits: so many problems, in principle soluble by the cryoscopic method, presented themselves—problems concerning the behaviour of strong acids other than nitric acid, of aromatic nitro-compounds, and of other organic oxygen compounds, in solvent sulphuric acid. The original research thus has become greatly extended, although only those results which are most relevant to the nitration problem are now being published.

There has been one general aim in all this work. Hitherto, despite important improvements of method, the cryoscopic study of ionic equilibria in sulphuric acid has never been raised above a semi-quantitative status; it has not previously been possible to calculate reliable equilibrium constants from the cryoscopic results. An attempt has been made to improve this position. In order to do so it has been necessary to go carefully into such questions as the precise value of the cryoscopic constant of sulphuric acid, the degree to which ionic solutions in sulphuric acid attain ideality, the self-ionisation of sulphuric acid, and the value of the equilibrium constant for the fundamental proton-transfer reaction between solvent sulphuric acid and solute water. These subjects occupy much of the first few papers of this series.

(1.2) *Previous Work on Cryoscopy in Sulphuric Acid.*—The earliest systematic measurements of the depression by solutes of the freezing point of sulphuric acid were those of Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257; 1908, **62**, 626; 1908, **65**, 41; 1909, **68**, 204; *Gazzetta*, 1909, **39**, i, 120; 1909, **39**, ii, 512; 1911, **41**, i, 645; *Ber.*, 1922, **55**, 953; 1930, **63**, 1782, 1789). He showed that the purity of the solvent sulphuric acid could not be adequately controlled by chemical analysis, and that the best criterion of its purity was the freezing point, which he found to have a maximum value of 10·46° (cf., however, Section 4), and to be sensitive to analytically undetectable amounts of water and sulphur trioxide. He discovered a number of substances which, on dissolution in sulphuric acid, had but little effect on its electrical conductivity; and they all gave about the same molal depression of the freezing point. He therefore assumed that they dissolved normally, that is, as simple non-electrolytes; and, from the freezing-point depressions which they gave, he deduced his value for the cryoscopic constant of sulphuric acid. Many solutes were found which considerably increased the electrical conductivity of sulphuric acid; and these gave larger molal depressions of the freezing point. Thus potassium hydrogen sulphate, water, alcohols, ethers, ketones, carboxylic acids, and amines gave about 1·5—2 times the normal depressions. Hantzsch assumed these compounds to dissolve with the formation of two ions, water and the organic oxygen compounds, as well as the amines, acting towards sulphuric acid as simple bases. Barium hydrogen sulphate, urea, and phthalic acid gave 2—2·5 times the normal depressions: and they were assumed to form three ions. Some substances, notably nitric acid and triphenylcarbinol, gave larger freezing-point depressions; and in these cases special explanations were suggested.

Similar measurements were recorded, largely in the same period, by Oddo and his collaborators (Oddo and Scandola, *Z. physikal. Chem.*, 1908, **62**, 243; 1909, **66**, 138; *Gazzetta*, 1908, **38**, i, 603; 1909, **39**, *i*, 569; 1909, **39**, ii, 1; 1910, **40**, ii, 163; Oddo and Cassalino, *ibid.*, 1917, **47**, ii, 200, 232; Oddo, *ibid.*, 1918, **48**, i, 17). They measured the cryoscopic constant of sulphuric acid in much the same way as Hantzsch had done, obtaining, however, somewhat different values. They also studied a wide range of organic and inorganic solutes and obtained results which, although broadly similar to those of Hantzsch, often differed quantitatively from his, essentially on account of the inaccurate experimental methods which constituted the best technique of that time. Some of Hantzsch's qualitative conclusions had to be altered: thus alcohols, which he had considered to behave as simple bases, were found by Oddo and Scandola to give a nearly three-fold depression of the freezing point, a clear indication that they become esterified with sulphuric acid (cf. Part VI). These authors were the first to recommend using as solvent, not pure sulphuric acid, but sulphuric acid containing a little water. However, they were not able to advance the correct reason for this procedure.

Reference will be made in acccompanying Parts of this series to the work of Poma (*J. Chim. physique*, 1912, **10**, 177) on the freezing points of sulphuric acid solutions of hydrogen sulphates (cf. Part IV), and to that of Robles and Moles (*Anal. Fís. Quím.*, 1934, **32**, 474; 1936, **34**, 331) on the depressions of the freezing point of sulphuric acid produced by nitric acid and perchloric acid (cf. Parts III and VI), and by the solutes water and sulphur trioxide (cf. Part II).

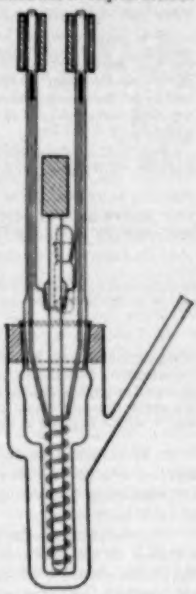
A definite improvement in experimental technique was achieved by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900) and by Treffers and Hammett (*ibid.*, 1937, **59**, 1788). Their freezing-point cell was of better design than those employed earlier. As solvent they used sulphuric acid containing a small amount of water, explaining that this was necessary in order to repress the self-ionisation of the solvent; and they corrected their freezing points for

supercooling. In their calculations they allowed for the non-proportionality of molality and mol.-fraction, and for the temperature-dependence of the latent heat of fusion of the solvent. For the cryoscopic constant they employed a value given by a calorimetric determination by Brönsted of the heat of fusion of sulphuric acid. They applied their methods mainly to the study of weak organic bases, and to the forms of ionisation undergone by carboxylic acids in solvent sulphuric acid.

The investigation of carboxylic acids and their esters has been carried further by Newman, Ruivila, and Garrett (*ibid.*, 1945, **67**, 704), Kuhn and Corwin (*ibid.*, 1948, **70**, 3370), and Kuhn (*ibid.*, 1949, **71**, 1575). Three other recent reports on the freezing points of sulphuric acid solutions have appeared, one by ourselves dealing with solutions of nitric acid, dinitrogen pentoxide, dinitrogen tetroxide, and dinitrogen trioxide (*Nature*, 1946, **158**, 480), one by Kuhn concerning the first two of these solutes and also ethyl nitrate (*J. Amer. Chem. Soc.*, 1947, **69**, 1974), and one by Price on the properties of siloxanes as solutes (*ibid.*, 1948, **70**, 871).

FIG. 1.

Freezing-point cell for solutions in sulphuric acid.



(1.3) *Apparatus and Experimental Procedure.*—In principle, the Beckmann method was used in order to measure freezing points, although the usual apparatus was considerably modified in order to prevent error due to the intrusion of water vapour, and, generally, to secure a satisfactory standard of accuracy.*

The freezing-point cell (see Fig. 1), which was similar in type to that used by Treffers and Hammett, was designed to allow the use of a convenient quantity of sulphuric acid, to secure adequate immersion of the thermometer, to permit efficient stirring, and to provide suitable means for the introduction of liquid or solid solutes; and, in all circumstances, to keep out unwanted moisture. The ground-in head of the cell carried all necessary fittings, *viz.*, two standard ground joints, one accommodating the thermometer and the other a stopper, and two sealed-in, vertical, tubes, closed at the top, to act as guides for the electromagnetic stirrer. The stirrer consisted of a glass spiral joined at the top of two vertical glass rods, to the upper end of each of which a closed glass tube containing a soft-iron rod was sealed. The stirrer was actuated by two solenoids, supported one on each of the guide-tubes, and fed by an intermittent direct current, the period of which was controlled by a mercury switch, rocked by a rotating cam, driven by an electric motor. It was found unnecessary to provide cooling jackets for the solenoids, which produced no appreciable thermal disturbance.

In the early stages of this work an ordinary Beckmann mercury thermometer was used. It was fitted to the freezing-point cell by means of rubber tubing impregnated with paraffin wax. This thermometer was later replaced by a platinum-resistance thermometer, with which all the final sets of measurements recorded in these papers were made. Small differences of temperature could be measured (to 0·001°) equally well with either thermometer; but the measurement of temperature in an absolute sense (to 0·01°) was made much easier by the use of the resistance thermometer. Furthermore, this thermometer was designed and built as part of the equipment, so that its dimensions were optimal; and it had, sealed on to its hard-glass sheath, a standard ground joint by which it could be fitted to the cell-head; it was a definite advantage to be able to avoid the use of rubber in the apparatus. Calibrated at the National Physical Laboratory, this thermometer had the resistance 30·0435 ± 0·0005 ohms at 0°, and 41·802 ± 0·001 ohms at 100°. The resistance of the thermometer, which was of the potential-lead type, was measured with the aid of a Smith's difference-bridge.

The opening in the cell-head, which normally accommodated a stopper, provided a way for the introduction of solutes with the aid of suitable delivery apparatus. In order to prevent the incursion of water vapour during measurements, it was found essential to grease all ground-joints; and for this purpose Apiezon M grease was used.

The freezing-point cell was supported in an air-jacket provided with an upward-sloping side-arm; and the air-jacket was surrounded by a water-bath containing a stirrer, a heater, and a cooling unit. The temperature of the bath could be quickly raised by the electric heater, or lowered by pumping cold alcohol through the cooling coils, and thus readily controlled to within 0·1°.

In order to make a series of freezing-point measurements, a weighed amount of sulphuric acid (about 120 g.) was introduced into the cell, and allowed to remain over-night, in order that any moisture present might be absorbed. By adjusting the temperature of the bath, the temperature of the sulphuric acid was then reduced until a supercooling of about 1·5° had been attained. The temperature of the bath was then brought to 1·2° ± 0·2° below the freezing point of the sulphuric acid, and crystallisation was

* The earlier stages of development of the methods described in this section were carried through by Professor J. Graham and Dr. E. R. A. Peeling, whose basic work is gratefully acknowledged.

started by touching the outside of the cell with a small piece of solid carbon dioxide, inserted by means of a holder down the side-arm of the air-jacket. The temperature just before crystallisation was taken as the supercooling temperature; and the steady maximum of temperature, reached after crystallisation, was accepted as the freezing point. The measurement could be repeated as often as desired. Similar measurements were made after the introduction of successive weighed amounts of the solute. It was found that, provided that any necessary thermometric corrections were applied, and also the correction for supercooling as noted in Section 1.4, the freezing point could be reproduced to within 0·002° even after the solution had been allowed to remain in the cell for several days—a clear proof that the cell was moisture-tight.

Liquid solvents were introduced with the aid of a weight-pipette, one arm of which was long enough to reach down almost to the surface of the sulphuric acid. Some granular solids were added by means of a kind of weight-burette, having a tap with a wide bore, and a long, wide stem, which could be closed with a cap for weighing. Solids which were difficult to handle thus were introduced as concentrated solutions in sulphuric acid by the use of the weight pipette.

In some experiments the solvent was sulphuric acid having the maximal freezing point. In others, indeed in most, it was sulphuric acid to which sufficient water had been added to suppress the self-ionisation of the pure acid.

(1.4) *The Correction for Supercooling.*—To each observed freezing point a correction for the supercooling of the solution has to be added. Let T_0 be the freezing point of the pure sulphuric acid, and T the true freezing point of the solution, so that $\theta = T_0 - T$ is the true depression of the freezing point. Let T_1 be the observed freezing point of the solution, so that $\theta_1 = T_0 - T_1$ is the observed depression. Let T_s be the supercooling temperature, so that $S = T_1 - T_s$ is the amount of supercooling. Then the required correction for the supercooling is $\delta T = T - T_1 = \theta_1 - \theta$, and we shall show that it has the value $\delta T = 0{\cdot}012S\theta_1$.

For, if the solute was dissolved in W g.-mols. of solvent before the crystallisation, but in only W_1 g.-mols. afterwards, then we have

$$\theta/\theta_1 = W_1/W$$

very approximately. Further, if ΔH^f is the molar heat of fusion of the solvent, and C_p^l is its molar heat capacity in the liquid state, then, considering the heat balance, we can write

$$\Delta H^f(W - W_1) = C_p^l SW$$

in sufficient approximation. Eliminating W and W_1 between these two equations, we obtain the following formula for the supercooling correction:

$$\delta T = \theta_1 - \theta = (C_p^l/\Delta H^f)S\theta_1$$

If we take the value 32·1 cal. g.-mol.$^{-1}$ deg.$^{-1}$, extrapolated from the data of Rubin (cf. Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, New York, 1944, p. 337), as the molar heat capacity of liquid sulphuric acid at its freezing point, and a figure 2605 cal. g.-mol.$^{-1}$, deduced in Section 2.5, for the molar heat of fusion of sulphuric acid, then we obtain for the coefficient $C_p^l/\Delta H^f$ the value 0·012 deg.$^{-1}$, which appears in the formula given above.

(1.5) *i-Factors and* ν*-Factors.*—Results relating to the lowering of the freezing point of a solvent by a solute have often been expressed in terms of what are called van't Hoff's *i*-factors, but confusion has arisen through the use, explicitly or implicitly, of incorrect interpretations of such factors.

The van't Hoff *i*-factor is correctly defined as the ratio of the actual depression caused by a solute in the freezing point of the solvent to the depression which would be found in an equimolal solution of an ideal, non-solvated, non-electrolyte. When van't Hoff introduced his *i*-factors, he intended them to cover all deviations of the behaviour of real solutions from the equations, based on his ideal osmotic-pressure law, which applied to ideal solutions. No question then arose as to the physical origin of the deviations. However, following Arrhenius, it became usual to consider *i* as equal to the number of kinetically separate particles (molecules or ions) which are produced by the addition to the solution of one molecule of the solute. This interpretation remained customary until Lewis and Randall pointed out that it could not be correct ("Thermodynamics," McGraw-Hill, New York, 1923, p. 341), and that, for example, a degree of dissociation thus deduced from an *i*-factor was not the thermodynamic degree of dissociation. We now understand that an *i*-factor, as properly defined, is an over-all result arising from both the numbers of the different kinds of particles, and the forces they exert, or, in other words, from the concentrations of solute particles and the departure of the solution from ideality. In general, the *i*-factor measures an almost inextricable mixture of these two effects, and, as we shall see in more detail presently, even if a solution were strictly ideal, the precise relation between the *i*-factor and the number of solute particles would always have a complicated form, excepting in the special case in which $i = 1$. In spite of all this, van't Hoff's *i*-factors have been used in comparatively recent years in the sense of Arrhenius's partly incorrect interpretation.

In work on solutions in such a solvent as sulphuric acid one's chief interest is usually in the number of the solute particles, rather than in the effects of the forces they exert. For this reason, and in order to avoid confusion, we shall introduce another symbol to represent the average number of kinetically separate, dissolved, particles (molecules or ions) that are produced by the addition to the solution of one molecule of solute, calling this number the ν-factor of the solute.

In discussions concerning freezing-point measurements of low accuracy, the numerical differences between *i*-factors and ν-factors are of no practical consequence. However, when computing with modern cryoscopic data, it is desirable, for practical reasons, that a clear distinction between the two quantities should be maintained.

Theoretically, the distinction between *i*-factors and ν-factors is fundamental. On the one hand, the *i*-factor expresses, in a complicated and inexact way, a thermodynamic property of the solvent in the solution. On the other, the ν-factor expresses simply and exactly, a molecular property of the solute in the solution.

Lewis and Randall knew that the factor *i* has no simple thermodynamic meaning; but they were obviously trying to find some meaning for it when they wrote: "At best the factor *i* gives the ratio of the lowering of the activity of the solvent to the lowering which would be produced by a normal undissociated substance." However, even this is not correct; though it would be correct to say that the factor *i* is *approximately* equal to the ratio of the change in the *logarithm* of the activity of the solvent to the change in this quantity which would be observed in an equimolal solution of an ideal non-electrolyte.* From this it will be apparent that the factor *i* retains no very useful meaning, even in relation to the solvent. It certainly has none in relation to the solute, the properties of which are best defined by means of its ν-factor and the activity coefficients of the dissolved species. This method preserves as clear a distinction as is possible between the effect of the number of the solute particles and the effects due to their forces.

(1.6) *Calculation of ν-Factors.*—In order to reduce the following calculation to the simplest possible form, we shall at the outset introduce a conclusion, which actually was reached only after a fairly extensive study of freezing points of solutions in sulphuric acid; and of necessity we shall defer until later the presentation of the supporting evidence. It was pointed out by Hammett and Deyrup (*loc. cit.*) that inter-ionic forces in sulphuric acid solutions must be unusually small. The present conclusion is that they are completely negligible. More specifically, it is concluded that, to the best standards of accuracy that we can attain experimentally, dilute solutions in sulphuric acid, even solutions of ionised solutes, can be considered ideal. This implies that inter-ionic activity effects are so weak as to require that the dielectric constant of sulphuric acid shall be very much greater than that of any solvent whose dielectric constant has yet been measured. Such a "ferroelectric" dielectric constant is not inconceivable, if we may assume co-operative orientation in suitably associated structures (and there is, of course, plenty of evidence of association). A direct test of this deduction is being undertaken by one of us (R. J. G.) in association with Dr. D. J. Millen. In the meantime we shall reduce our cryoscopic results on the basis that the solutions can be treated as ideal, *i.e.*, that the relevant activity coefficients may be set equal to unity. It should perhaps be stated here that the assumption of ideality does not wipe out the numerical differences between ν-factors and *i*-factors (except for dilute solutions of a non-solvated non-electrolyte, for which $\nu = i = 1$). This will become clearer as we proceed to calculate ν.

Consider the equilibrium between the pure solid solvent and solutions of variable concentration at a constant pressure of one atmosphere. Let us denote activities by a, mol.-fractions by N, and molalities by m, with subscripts 1 and 2 referring to the solvent and solute, respectively. The basic equation for the variation of the activity of the solvent as the freezing point varies is

$$\mathrm{d} \ln a_1/\mathrm{d}T = \Delta H^f/RT^2;$$

but, in view of our conclusion concerning the ideality of the solutions in which we are interested, we can replace this equation by the following:

$$\mathrm{d} \ln N_1/\mathrm{d}T = \Delta H^f/RT^2$$

* This follows from a consideration of the equation $\mathrm{d} \ln a_1/\mathrm{d}T = \Delta H^f/RT^2$, where a_1 is the activity, and H^f is the heat of fusion, of the solvent in a solution of freezing-point T. Comparing two such equations, one for a solution of a real solute, and the other for an equimolal solution of an ideal solute, we derive the statement in the text by taking the right-hand sides as equal. A general approximation of this form involves neglecting all terms after the first in the expansion of $\Delta H^f/RT^2$ about its value in the pure solvent, $\Delta H_0^f/RT_0^2$, in powers of the freezing-point depression $T_0 - T$.

Since we usually express the composition of solutions in terms of the molality of the solute, rather than the mol.-fraction of the solvent, it becomes convenient to transform this equation as follows :

$$dT/dm_2 = (RT^2/\Delta H')(d \ln N_1/dm_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We have now to calculate the two factors on the right, so let us consider the factor $d \ln N_1/dm_2$. In many of our experiments the solvent was pre-treated with a small amount of water before addition of the solute in which we were interested; and for this and other reasons it is convenient here to consider the general case in which two solutes A and B are employed. Suppose that one molecule of the solute A interacts with s_1 molecules of sulphuric acid to form a total number ν_1 of dissolved ions and non-ionised molecules, and that one molecule of solute B reacts with s_2 molecules of sulphuric acid to give ν_2 dissolved ions and molecules :

$$A + s_1H_2SO_4 = pP + qQ + rR + \ldots\ldots$$
$$p + q + r + \ldots = \nu_1$$
$$B + s_2H_2SO_4 = xX + yY + zZ + \ldots\ldots$$
$$x + y + z + \ldots = \nu_2$$

Then, if m_1 is the molality of the solute A and m_2 that of B, we may write the following expression for N_1 :

$$N_1 = (m_1 - s_1m_1 - s_2m_2)/[m_1 + (\nu_1 - s_1)m_1 + (\nu_2 - s_2)m_2]$$

From this, by differentiation, we obtain the result

$$\frac{d \ln N_1}{dm_2} = -\frac{s_2}{m_1}\left\{1 + \frac{(2s_1 - \nu_1)\nu_2m_2 + (\nu_2s_1 + \nu_1s_2 - \nu_1\nu_2)m_1}{\nu_2m_1}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

provided that we neglect second and higher orders in the small quantities m_2/m_1 and m_2/m_1.

The calculation of the factor $RT^2/\Delta H'$ involves taking account of the variation of $\Delta H'$ with T. If $\Delta H_0'$ is the molar heat of fusion of pure sulphuric acid, *i.e.*, its latent heat at the temperature T_0, then the latent heat $\Delta H'$ at the temperature T is to be computed by integrating Kirchhoff's equation

$$\delta(\Delta H')/\delta T = C_p' - C_p{}^s = \Delta C_p$$

where C_p' and $C_p{}^s$ are the molar heat capacities of liquid and solid sulphuric acid, respectively, at the freezing point. Disregarding, as we may with sufficient approximation, the temperature dependence of ΔC_p, we find for the integral,

$$\Delta H_0' - \Delta H' = \Delta C_p(T_0 - T) = \Delta C_p\theta ;$$

and from this, by neglecting second- and higher-order terms in the small quantities $(\Delta H_0' - \Delta H')/\Delta H_0'$ and θ/T_0, we obtain

$$\frac{RT^2}{\Delta H'} = \frac{RT_0{}^2}{\Delta H_0'}\left\{1 - \frac{2\theta}{T_0} + \frac{\Delta C_p\theta}{\Delta H_0'}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting from equations (2) and (3) in equation (1) and remembering that $dT = -d\theta$, we find

$$\frac{d\theta}{dm_1} = \nu_2 \cdot \frac{RT^2}{m_1\Delta H_0'} \cdot \left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0'}\right)\theta\right\} \cdot \left\{1 + \frac{(2s_1 - \nu_1)\nu_2m_2 + (\nu_2s_1 + \nu_1s_2 - \nu_1\nu_2)m_1}{\nu_2m_1}\right\}$$

The equation for a small but finite change $\Delta\theta$ in the freezing-point depression, caused by a small but finite change Δm_1 in the molality of solute A, is similar, except that, on the left, the ratio $\Delta\theta/\Delta m_1$ will replace the differential coefficient, and, on the right, the mean freezing-point depression $\bar{\theta}$, and the mean molality $\overline{m_2}$ of solute A, over the finite interval, will replace θ and m_2 respectively.

The factor $RT_0{}^2/m_1\Delta H_0'$ is a constant of the solvent, *viz.*, the cryoscopic constant k_f. Another constant of the solvent is m_1, which has the value $1000/98{\cdot}076 = 10{\cdot}196$ g.-mol. kg.$^{-1}$. The factor $(2/T_0) - (\Delta C_p/\Delta H_0')$ may be computed to be $0{\cdot}0035$ deg.$^{-1}$ from the following values : $\Delta H_0' = 2605$ cal. g.-mol.$^{-1}$ (cf. Section 3), $T_0 = 10{\cdot}36°$ c. $= 283{\cdot}5°$ K. (cf. Section 4), and $\Delta C_p = 9{\cdot}2$ cal. g.-mol.$^{-1}$ deg.$^{-1}$ (from Rubin's calorimetric data, cf. Yost and Russell, *op. cit.*). Thus, retaining small quantities in the first order only, we can express the freezing-point equation in the following form :

$$\frac{\Delta\theta}{\Delta m_1} = \nu_2k_f\left[1 - 0{\cdot}0035\bar{\theta} + \left\{\frac{(2s_1 - \nu_1)\nu_2\overline{m_2} + (\nu_2s_1 + \nu_1s_2 - \nu_1\nu_2)m_1}{\nu_2m_1}\right\}\right] \quad . \quad . \quad (4)$$

In the special case in which the solute B is water in a low concentration, we may assume, with sufficient accuracy for our present purpose, a reaction according to the equation

$$H_2O + 2H_2SO_4 = H_3O^+(H_2SO_4) + HSO_4^-$$

It is shown in Part II that in dilute solution in sulphuric acid water ionises almost completely according to an equation of this general type, one of the formed ions being solvated with approximately one molecule of sulphuric acid. Thus we may substitute $s_2 = 2$ and $\nu_2 = 2$ in equation (4), with the following result:

$$\frac{\Delta\theta}{\Delta m_2} = \nu_2 k_f \left[1 - 0{\cdot}0035\bar{s} + \left\{\frac{(2s_2 - \nu_2)\nu_2\bar{m}_2 + 2s_1 m_2}{\nu_2 m_2}\right\}\right] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation gives the change in the freezing-point depression, $\Delta\theta$, caused by a small change Δm_2 in the molality of the experimental solute A, in the presence of a small amount of water of fixed molality m_2. This is the equation which, in this series of papers, has been used for many of the calculations of ν-factors from cryoscopic data, although for some calculations other forms of the general equation (4) have been employed.

Hammett and Deyrup (*loc. cit.*) used equations which, apart from a minor numerical difference, may be regarded as special cases of equation (5). They called the quantity which we term ν_2, the van't Hoff factor i; but it will be evident that, even with the assumption of ideality, the factor ν_2, and the van't Hoff factor i as properly defined, are in general not numerically identical. Two reasons for this appear when we examine equation (5). First, the trinomial [ ] contains ν_2; and for that reason alone the trinomial will not, in general, cancel out when, with the object of computing the true factor i for an electrolytic solute, we calculate the ratio of $\Delta\theta/\Delta m_2$ for the solute ($\nu_2 \neq 1$) to $\Delta\theta/\Delta m_2$ for an ideal, non-solvated, non-electrolyte ($\nu_2 = 1$). Secondly, the expression [ ] also contains s_2; wherefore solvation, even the solvation of a non-electrolyte, will alter i, though it cannot alter ν_2.

(2) *Cryoscopic Constant of Sulphuric Acid.*

(2.1) *Previous Determinations of the Cryoscopic Constant.*—The determination of an accurate value for the cryoscopic constant of sulphuric acid is a matter of some difficulty. There are two ways of obtaining the cryoscopic constant of a solvent: either it can be measured by observation of the depression of freezing point caused by a solute which is believed not to ionise or react in any way with the solvent; or it can be calculated from the calorimetrically determined latent heat of fusion of the solvent. Both methods have been used in the case of sulphuric acid; but it appears that the number of substances which are appreciably soluble in sulphuric acid, but do not react with it, is very small; and, as we shall note later, there seems to be no reliable calorimetric value for the heat of fusion of sulphuric acid.

Previous investigators have employed considerably varying values of the cryoscopic constant of sulphuric acid. Hantzsch used the value 7·00 deg. g.-mol.$^{-1}$ kg., which was an average figure, deduced from freezing-point depressions given by the following solutes: trichloroacetic acid, 2 : 4-dinitromesitylene, 1 : 3 : 5-trinitrobenzene, 2 : 4 : 6-trinitrotoluene, picric acid, phthalic anhydride, oxalic acid, and methyl sulphate. He found that all these substances had little effect on the electrical conductivity of sulphuric acid, and that they all gave about the same molal depression of the freezing point.

Oddo and Scandola adopted the value 6·81 deg. g.-mol.$^{-1}$ kg., which they derived from the freezing-point depressions given by the solutes phosphorus oxychloride and sulphuryl chloride. Later, Oddo changed this figure to 6·9 deg. g.-mol.$^{-1}$ kg. This was an average value, in computing which account was taken of cryoscopic data relating to the solutes trichloroacetic acid, 1 : 3 : 5-trinitrobenzene, and picric acid, solutes which had been used by Hantzsch. Oddo pointed out that the employment of phthalic anhydride, oxalic acid, and methyl sulphate, which had also been used by Hantzsch, led to values of the cryoscopic constant which depended on the concentration of the solute; and that it was therefore to be presumed that these solutes reacted with sulphuric acid.

Hammett and Deyrup derived the mean values 6·00, 6·26, and 6·11 deg. g.-mol.$^{-1}$ kg. from cryoscopic measurements with the solutes trichloroacetic acid, 1 : 3 : 5-trinitrobenzene, and picric acid, respectively. Robles and Moles obtained an average value of 6·55 deg. g.-mol.$^{-1}$ kg. from the freezing-point depressions produced by trichloroacetic acid, picric acid, nitrobenzene, and 2 : 4 : 6-trinitrotoluene. They surveyed the values of the cryoscopic constant given by previous workers—values ranging from 6·0 to 7·0 deg. g.-mol.$^{-1}$ kg.—and concluded in favour of a best value of 6·56 deg. g.-mol.$^{-1}$ kg.

The large divergencies between these figures arise in part from errors of experimental method, such as failure to correct for supercooling, failure to control the suppression of the self-ionisation of the solvent, and failure to prevent intrusions of moisture; but, as will be established in Section 2.2 of this paper, and particularly in Part VII, they are due much more to the circumstance that almost all the solutes employed behave as weak bases, becoming ionised in varying degrees, whilst some also react in other ways with the solvent.

As for the second method of determining the cryoscopic constant, the following values of the molar heat of fusion of sulphuric acid are recorded:

Berthelot (*Compt. rend.*, 1874, **78**, 716)	860	cal. g.-mol.$^{-1}$
Pickering (*J.*, 1890, **57**, 385; *Proc. Roy. Soc.*, 1891, **49**, 11)	2355	,,
Knietsch (cf. Hantzsch, *Z. physikal. Chem.*, 1908, **61**, 262)	2236	,,
,, (recalculated by Brönsted, *q.v.*)	1803	,,
Brönsted (*Z. physikal. Chem.*, 1909, **68**, 693)	2550	,,
Rubin (cf. Yost and Russell, *op. cit.*)	2561	,,

Pickering's figure for the latent heat of fusion leads to a value 6·65 deg. g.-mol.$^{-1}$ kg. for the cryoscopic constant. Brönsted's latent heat value gives 6·15 deg. g.-mol.$^{-1}$ kg. This is the figure which Hammett and Deyrup adopted in their work, considering it to be in satisfactory agreement with, and therefore to be the value indicated by, the various determinations which they had made by direct observation of freezing-point depressions. From Rubin's latent heat value one may calculate the figure 6·12 deg. g.-mol.$^{-1}$ kg. for the cryoscopic constant.

Although Rubin's value of the heat of fusion is undoubtedly the most accurate yet obtained, it cannot be correct; for the freezing point of the acid used was only 10·31°, whereas the freezing point of sulphuric acid has been found in this investigation to be 10·36° (Section 4). Small amounts of impurities may lead to quite large errors in calorimetric measurements of the latent heat of fusion, because they cause pre-melting, for which it is difficult to make an accurate correction. It may well be supposed that Rubin's acid contained a small amount of either sulphur trioxide or water, for, as has been mentioned already, it is impossible accurately to control the composition of sulphuric acid by chemical analysis, or to obtain the pure acid by any method other than the adjustment of its freezing point. We may conclude, therefore, that Rubin's latent heat value, although it is the highest yet recorded, is nevertheless too low, and that the cryoscopic constant to which it leads is correspondingly high.

(2.2) *Cryoscopic Evaluation of the Constant (First Method).*—In our search for substances which would dissolve unchanged in sulphuric acid, and thus permit a determination of the cryoscopic constant of that solvent by direct observation of their effect on its freezing point, we examined the following solutes: sulphuryl chloride, chlorosulphonic acid, nitromethane, 2 : 4 : 6-trinitrotoluene, phosphorus oxychloride, and methyl sulphate. With each solute a number of experiments were carried out using sulphuric acid solvents of different composition: we used both sulphuric acid having the maximum freezing point, and sulphuric acid of which the freezing point had been reduced by the addition of different small concentrations of water. The results of the experiments on four of the solutes are recorded in Tables I—IV; the figures for the other two solutes are given in an accompanying paper (Part VII).

A selection of these results is here shown as plots of the freezing-point depression against the molality of the solute. The plot for sulphuryl chloride is seen in Fig. 2; independently of the water-content of the solvent, all the points lie on one curve. The data for chlorosulphonic acid are exhibited in Fig. 3: these points lie on a series of divergent curves, whose positions are dependent on the water-content of the solvent. The analogous plots for the other four solutes are not reproduced; for each of these solutes, the representative points, for sets of readings with solvents having various fixed concentrations of water, lie either on only slightly separated curves, or to a very close approximation on a single curve.

A complete and accurate graphical comparison of the behaviour of all these substances requires a plot on a larger scale than would be suitable for reproduction; but it is a useful preliminary step to make a comparison in the following approximate manner, namely, by reading off from diagrams, such as are shown in Figs. 2 and 3, the depressions of freezing point given by a 0·1 molal solution of each solute. The result of such a comparison is shown in Table V. The concentration 0·1 molal is taken because, as we shall see presently, effects due to non-ideality are negligible up to concentrations at least as high as that. The depression of freezing point caused by a solute in 0·1 molal concentration is, of course, not exactly equal to one-tenth of the value of the cryoscopic constant, k_f, which would be obtained in an application of equation (4) to the experimental data; but the differences between one depression and another

for this fixed molality will reflect fairly closely the differences which would be found in values thus calculated for the cryoscopic constant.

TABLE I.

Freezing points of solutions of sulphuryl chloride in sulphuric acid.

Molality of SO_2Cl_2 (Δm_2).	F. p.† (° c.).	k_f.*	Molality of SO_2Cl_2 (Δm_2).	F. p. (° c.).	k_f.*	Molality of SO_2Cl_2 (Δm_2).	F. p. (° c.).	k_f.*
Expt. No. 57. Molality of H_2O (m_1) = 0·005.			Expt. No. 56. Molality of H_2O (m_1) = 0·015.			Expt. No. 42. Molality of H_2O (m_1) = 0·020.		
—	10·342	—	—	10·291	—	—	10·262	—
0·0350	10·131	6·04	0·0256	10·137	6·02	0·0757	9·814	5·94
0·0645	9·961	5·93	0·0608	9·923	6·06	0·0880	9·740	5·96
0·0923	9·798	5·94	0·0909	9·743	6·00	0·1190	9·554	5·99
0·1363	9·546	5·88	0·1181	9·588	5·98	0·1425	9·429	5·91
0·1693	9·364	5·84	0·1517	9·408	5·86	0·1661	9·297	5·86
						0·1896	9·169	5·82
Expt. No. 43. Molality of H_2O (m_1) = 0·025.						Expt. No. 44. Molality of H_2O (m_1) = 0·032.		
—	10·211	—	0·1822	9·161	5·83	—	10·165	—
0·0491	9·818	5·99	0·1989	9·073	5·79	0·0288	9·993	5·93
0·1020	9·619	5·84	0·2302	8·903	5·77	0·0553	9·834	6·00
0·1335	9·442	5·81				0·0754	9·720	5·93

* k_f (in the units deg. g.-mol.$^{-1}$ kg.) is calculated from equation (5) with the substitutions $s_1 = 0$ and $\nu_2 = 1$.

† Throughout these papers, ° c. means degrees Celsius on the international scale of temperature.

TABLE II.

Freezing points of solutions of chlorosulphonic acid in sulphuric acid.

Molality of Cl·SO_3H (Δm_2).	F. p. (° c.).	k_f.*	Molality of Cl·SO_3H (Δm_2).	F. p. (° c.).	Molality of Cl·SO_3H (Δm_2).	F. p. (° c.).
Expt. No. 47. Molality of H_2O (m_1) = 0·003.			Expt. No. 48. Molality of H_2O (m_1) = 0·034.		Expt. No. 46. Molality of H_2O (m_1) = 0·081.	
—	10·347	—	—	10·131	—	9·631
—	10·135	—	0·0556	9·746	0·0664	9·368
0·0440	9·874	5·97	0·0982	9·608	0·0998	9·242
0·0995	9·544	6·00	0·1312	9·434	0·1501	9·008
0·1438	9·280	6·02	0·1704	9·225	0·1926	8·805
0·1996	8·963	5·98				

* Calculated from equation (5) with the substitutions $s_1 = 0$ and $\nu_2 = 1$ (units as in Table I).

TABLE III.

Freezing points of solutions of phosphorus oxychloride in sulphuric acid.

Expt. No. 51. Freezing point of solvent = 10·354°. Molality H_2O = 0·00.				Expt. No. 49. Freezing point of solvent = 10·150°. Molality H_2O = 0·035.			
Molality $POCl_3$.	F. p. (° c.).	Molality $POCl_3$.	F. p. (° c.).	Molality $POCl_3$.	F. p. (° c.).	Molality $POCl_3$.	F. p. (° c.).
0·0168	10·249	0·0924	9·777	0·0219	10·002	0·0878	9·559
0·0594	9·996	0·1369	9·471	0·0586	9·767	0·1178	9·252

TABLE IV.

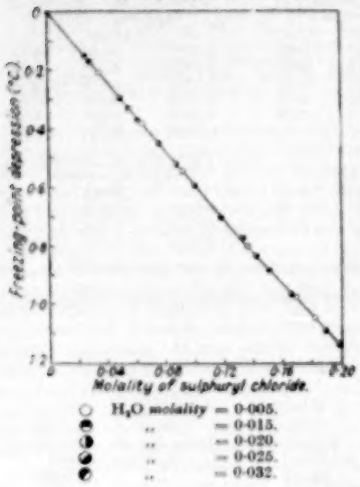
Freezing point of solutions of methyl sulphate in sulphuric acid.

Expt. No. 55. Freezing point of solvent = 10·348°. Molality H_2O = 0·00.				Expt. No. 53. Freezing point of solvent = 10·186°. Molality H_2O = 0·031.			
Molality $(CH_3)_2SO_4$.	F. p. (° c.).	Molality $(CH_3)_2SO_4$.	F. p. (° c.).	Molality $(CH_3)_2SO_4$.	F. p. (° c.).	Molality $(CH_3)_2SO_4$.	F. p. (° c.).
0·0161	10·244	0·0735	9·866	0·0333	9·974	0·1309	9·252
0·0456	10·054	0·1017	9·671	0·0724	9·710	0·1645	9·061
				0·1053	9·487		

It will be clear from Table V, and from such graphs as are reproduced here, that the differences between the freezing-point depressions given by the various solutes in identical concentration are much larger than could be attributed to experimental error. The same inference can, indeed, be derived from a comparison of the results obtained by earlier workers: notwithstanding the larger experimental error, it is impossible to avoid the conclusion that the

FIG. 2.

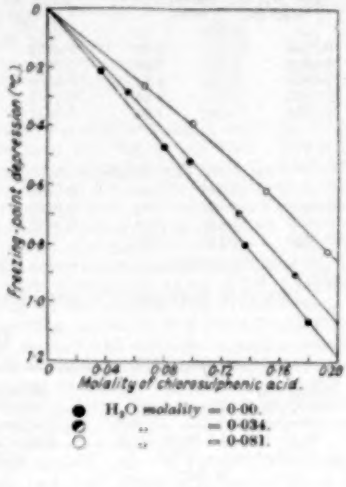
Depression of the freezing point of sulphuric acid by sulphuryl chloride.



○ H_2O molality = 0·005.
◓ ,, = 0·015.
◑ ,, = 0·020.
◕ ,, = 0·025.
● ,, = 0·032.

FIG. 3.

Depression of the freezing point of sulphuric acid by chlorosulphonic acid.



● H_2O molality = 0·00.
◕ ,, = 0·034.
○ ,, = 0·081.

TABLE V.

Depression of the freezing point of sulphuric acid by solutes in 0·1 molal concentration.

Solute.	Expt.	Molality H_2O.	Depression (m = 0·1).
Sulphuryl chloride	all	0·00—0·03	0·590°
Chlorosulphonic acid	47	0·00	0·590
Nitromethane	32	0·04	0·625
2 : 4 : 6-Trinitrotoluene	39	0·07	0·655
Methyl sulphate	55, 53	0·00—0·03	0·660
Phosphorus oxychloride	51	0·00	0·675

differences of behaviour between the different substances are real. This being so, we cannot be content to take an average from such results when computing the cryoscopic constant, or to adopt any other procedure for obtaining it which leaves the discrepancies unexplained.

Two of our solutes, sulphuryl chloride and chlorosulphonic acid, but the latter only in sulphuric acid of maximal freezing point, gave the same freezing-point depression at the concentration 0·1 molal; and it is significant that, of all the substances examined, these two gave the smallest depressions. As none of our solutes is likely to be associated in dilute solution in sulphuric acid, the most obvious conclusion is that sulphuryl chloride and chlorosulphonic acid dissolve unchanged, whereas all the other solutes ionise or react with the solvent in some other way.

From the freezing-point depressions given by sulphuryl chloride in pure and in slightly aqueous sulphuric acid, and by chlorosulphonic acid in pure sulphuric acid, we have calculated the cryoscopic constants of sulphuric acid, using equation (5) with the substitutions $z_s = 0$ and $\nu_s = 1$. The results of these calculations are given in the last columns of Tables I and II.

It is necessary to consider the limits of concentration within which the solutions, from whose freezing points we compute the cryoscopic constant, can be considered ideal. The curve

(Fig. 2) for the depression of freezing point given by sulphuryl chloride agrees very closely indeed up to a concentration of 0·12 molal with the almost linear form of curve required by equation (4) for an ideal solute; and, accordingly, we may conclude that over this range of concentration the solutions are accurately ideal. Above this limit the curve swings away slightly from the theoretical form; and this we interpret as an indication of non-ideality in these more concentrated solutions. The direction of the effect is such as might indicate a slight tendency to association of the solute; alternatively, it might point to a slight reduction in the ionising power of the medium as a whole, with consequent diminution in the extent of the ionisation of its constituents, sulphuric acid and water. We need not here discuss the very exact ideality of the dilute solution—*i.e.*, the apparent insignificance in sulphuric acid of the long-range forces between solute particles, which often produce appreciable non-ideality in dilute solution—because we shall presently encounter the same phenomenon in the much more remarkable case of ionic solutes. For chlorosulphonic acid, the range of ideality seems to extend at least to 0·20 molal.

We may then accept for consideration those calculated values of the cryoscopic constant which are based on measurements with solutions of sulphuryl chloride and chlorosulphonic acid having concentrations within the indicated ranges of ideality. These values are assembled in Table VI. They indicate a figure, 5·98 deg. g.-mol.$^{-1}$ kg., for the constant, a value which we shall confirm in other ways.

TABLE VI.

Determination of the cryoscopic constant (k_f) *of sulphuric acid.*

(Method 1.)

Solute (and range of its molality).	Expt. no.	Molality of water.	k_f (deg. g.-mol.$^{-1}$ kg.).	Mean k.
Sulphuryl chloride (0<*m*<0·12)	57	0·005	5·97	5·98
	56	0·015	6·02	
	42	0·020	5·96	
	43	0·025	5·99	
	44	0·032	5·95	
Chlorosulphonic acid (0<*m*<0·20)	47	0·003	5·99	5·99
				Mean 5·98

The behaviour of the other investigated solutes requires comment. The nature of the influence of water on the freezing-point depression produced by chlorosulphonic acid has not yet been unequivocally elucidated. There are two conceivable reactions between chlorosulphonic acid and water; and the first of them is almost certainly in operation, whilst the second might be. The first is an acid-to-base proton transfer:

$$Cl{\cdot}SO_3H + H_2O = Cl{\cdot}SO_3^- + H_3O^+$$

Since water is largely ionised as a binary electrolyte (cf. Part II), this process, if complete, would simply replace one binary electrolyte by another; and hence no change of freezing point would result when chlorosulphonic acid is added, until the amount of it began to exceed that of the originally present water. The second possible reaction with water involves hydrolytic separation of chlorine from the chlorosulphonic acid molecule:

$$Cl{\cdot}SO_3H + H_2O = HCl + H_2SO_4$$

The cryoscopic behaviour of hydrogen chloride has not yet been determined, but under any hypothesis, the above hydrolysis, if complete, would cause the addition of chlorosulphonic acid to a sulphuric acid solution, already containing water, to produce either no change of freezing point, or a rise of freezing point, until the concentration of the added chlorosulphonic acid begins to exceed that of the water. The fact that, in the presence of water, we observe a depression, though a reduced one, from the commencement of the addition of the chlorosulphonic acid, must be interpreted to mean that the above reactions at best proceed only partly in the forward direction.

As the desirability of adding water to the sulphuric acid solvents employed for cryoscopic measurements is often emphasised, it may be noted here that the need for this precaution does not apply to measurements on non-ionising solutes. If a solute does not ionise, and does not react in any way with either the sulphuric acid or the water, then the presence of water in small amount cannot make any difference to the cryoscopic behaviour of the solute. This is illustrated

in the example of sulphuryl chloride. If a solute does not ionise, and does not react in any way with the sulphuric acid, but does react with the water, then we cannot hope to get correct cryoscopic results unless the water is omitted. This is the situation with chlorosulphonic acid, for instance. The object of adding water has significance in the case of basic solutes, and ionising salts, because they generate the hydrogen sulphate ion, which is one of the ions produced by the self-ionisation of sulphuric acid. As the hydrogen sulphate ion, generated by a basic solute or an ionising salt, would repress the self-ionisation of the solvent, thereby disturbing the change of freezing point due to the solute, it is better largely to repress the self-ionisation initially, by the addition of a base, such as water, so that the solute under investigation can itself have little further effect in that direction. This type of case is exemplified by the nitro-compounds mentioned below; and there are some further illustrations in Sections 2.3 and 2.4. Of course, the originally added base need not be water: any strong base, such as benzoic acid or acetophenone, and, still more simply, any ionised sulphate or hydrogen sulphate will do what is necessary.

The choice of an agent for so modifying the solvent that errors caused by changes in its self-ionisation on addition of the experimental solute are avoided is really a more complicated matter than would appear from the explanation given above. It will be shown in Part IV that sulphuric acid suffers two forms of self-dissociation; water has an advantage over other possible agents in that it suppresses both. It will be shown in Part II, however, that water does not behave as an infinitely strong base in sulphuric acid; therefore water suffers from the disadvantage that its own degree of ionisation may be altered by the experimental solute. When this solute produces a liberal supply of one or more of the dissociation products of the solvent, then the self-dissociation of the latter can be suppressed or stabilised by the use of some of the experimental solute for this purpose.

We return to the discussion of the data in the preceding Tables. Of the other substances investigated, all of which gave greater depressions of the freezing point than did sulphuryl chloride or chlorosulphonic acid, two, namely, nitromethane and 2 : 4 : 6-trinitrotoluene, will be considered in detail in Part VII. It will there be shown that these and other nitro-compounds, including those used by all the earlier workers in their attempts to determine the cryoscopic constant, behave as weak bases in sulphuric acid, ionising to varying extents according to the general equation

$$R{\cdot}NO_2 + H_2SO_4 = R{\cdot}NO_2H^+ + HSO_4^-$$

Phosphorus oxychloride gave a freezing-point depression, which not only varied quite appreciably with the water content of the solvent, but also increased with the time. The readings of the freezing point which are here recorded as given by phosphorus oxychloride, were actually the steady values attained in each case several hours after the addition of the solute. It is clear from this alone that phosphorus oxychloride undergoes some form of solvolysis; and, of course, it may behave as a weak base, or its solvolysis products may behave as weak bases, in addition.

Oddo and Scandola first suggested (*Gazzetta*, 1910, **40**, ii, 163) that methyl sulphate undergoes reaction with sulphuric acid, and the present results give support to that idea. Here one suspects reversible solvolysis to methyl hydrogen sulphate. Methyl sulphate may act as a weak base in addition (cf. Part VII).

Of the other substances which were used by the earlier workers for the purpose of determining the cryoscopic constant, trichloroacetic acid and phthalic anhydride almost certainly behave as weak bases. They will be discussed in a later Part of this series. Presumably oxalic acid also behaves as a base, as do almost all carboxylic acids; but in any case oxalic acid decomposes in sulphuric acid.

The measurements of electrical conductivity on which Hantzsch relied in deriving his conclusion that the solutes he used were non-electrolytes have little significance. Pure sulphuric acid is considerably self-ionised, and therefore has a substantial electrical conductivity. The addition of a weak base, which, besides providing a limited number of new ions, suppresses the ionisation of the solvent, is not expected to increase the conductivity very greatly. Actually, small increases, such as might be expected, were observed by Hantzsch in several cases.

It would, of course, be desirable to have measurements of the depression of the freezing point of sulphuric acid by other non-reacting, non-ionising substances; but nearly all such substances are insoluble. It appears that liquid sulphuric acid possesses a very considerable amount of structure (as is indicated by its low vapour pressure and high viscosity), the molecules being held together in large groups by strong hydrogen bonds; and that such groups cannot in

general be broken into by a molecule unable to exert the strong forces of reaction or ionisation. It seems significant that the only soluble, non-reacting, non-ionising compounds that we have discovered have molecules which are similar in their general framework to the molecule of sulphuric acid, and are capable of participating in hydrogen bonds: such molecules may, perhaps, be pictured as replacing a sulphuric acid molecule in liquid sulphuric acid without producing more than a slight local fault in the structure.

(2.3) *Cryoscopic Evaluation of the Constant (Second Method).*—It is not customary to employ salts as solutes for the purpose of evaluating a cryoscopic constant, because ionic interactions extend over considerable distances, and thus tend to produce non-ideality in quite dilute solutions. However, it transpires that in solvent sulphuric acid these electrostatic non-ideality effects are extremely small over ranges of concentration amply sufficient to permit good cryoscopic measurement; this peculiarity of sulphuric acid renders the use of salts entirely feasible.

We have used two salts, *viz.*, potassium sulphate and ammonium sulphate. We assume that, when dissolved in sulphuric acid, they are completely converted into the corresponding hydrogen sulphates. The chemical equation for the conversion being, *e.g.*,

$$K_2SO_4 + H_2SO_4 = 2K^+ + 2HSO_4^-$$

we must expect, if we disregard certain disturbances noted below, to calculate the cryoscopic constant k_f from our results by means of equation (5) with the substitutions $s_2 = 1$ and $\nu_2 = 4$.

Since we are relying in part upon hydrogen sulphate ions to produce the measured depression of the freezing point, it is necessary, as has been mentioned above, to control the self-ionisation of the sulphuric acid. This has been done in two ways. We first give the results of experiments in which added water was employed for the purpose. They are contained in Tables VII and VIII, and are shown graphically in Figs. 4 and 5.

TABLE VII.

Freezing points of solutions of potassium sulphate in aqueous sulphuric acid.

K_2SO_4 (Δm_2).	$\Delta\theta$. (uncorr.).	$\Delta\theta$ (corr.). $n = 0.$	$n = 1.$	$n = 2.$	$n = 3.$	k_f (deg. g.-mol.$^{-1}$ kg.). $n = 0.$	$n = 1.$	$n = 2.$	$n = 3.$
Expt. 86 (molality H_2O, $m_0 = 0{\cdot}048$. F. p. of treated solvent, 9·990° c.):									
0·0085	0·204°	0·210°	0·208°	0·207°	0·207°	6·14	6·05	6·00	5·95
0·0169	0·405	0·416	0·413	0·411	0·410	6·15	6·04	5·97	5·89
0·0239	0·563	0·577	0·574	0·571	0·569	6·06	5·97	5·88	5·77
0·0444	1·069	1·093	1·088	1·083	1·079	6·18	6·07	5·96	5·81
0·0585	1·408	1·439	1·433	1·426	1·420	6·19	6·09	5·94	5·78
0·0667	1·612	1·647	1·640	1·633	1·626	6·22	6·09	5·95	5·77
0·0844	2·051	2·096	2·087	2·077	2·068	6·27	6·12	5·96	5·75
Expt. 63 (molality H_2O, $m_0 = 0{\cdot}056$. F. p. of treated solvent, 9·901° c.):									
0·0182	0·438	0·450	0·447	0·445	0·443	6·19	6·09	6·01	5·94
0·0286	0·680	0·697	0·694	0·692	0·689	6·11	6·02	5·92	5·83
0·0394	0·948	0·972	0·967	0·962	0·957	6·20	6·08	5·97	5·85
0·0527	1·266	1·296	1·290	1·284	1·277	6·19	6·06	5·93	5·82
Expt. 85 (molality H_2O, $m_0 = 0{\cdot}045$. F. p. of treated solvent, 10·022° c.):									
0·0499	1·198	1·225	1·220	1·214	1·208	6·17	6·06	5·95	5·84
0·0590	1·429	1·461	1·454	1·448	1·441	6·24	6·10	5·98	5·85
0·0700	1·701	1·738	1·730	1·723	1·715	6·26	6·11	5·97	5·85
0·0803	1·960	2·003	1·994	1·985	1·976	6·30	6·14	5·97	5·85

TABLE VIII.

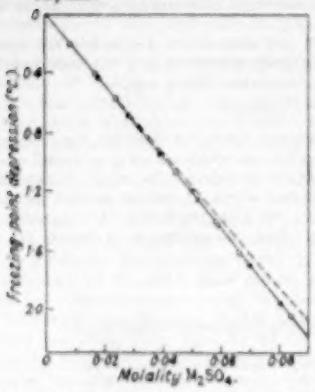
Freezing points of solutions of ammonium sulphate in aqueous sulphuric acid.

Am_2SO_4 (Δm_2).	$\Delta\theta$ (uncorr.).	$\Delta\theta$ (corr.). $n = 0.$	$n = 1.$	$n = 2.$	k_f (deg. g.-mol.$^{-1}$ kg.). $n = 0.$	$n = 1.$	$n = 2.$
Expt. 123 (molality water, $m_0 = 0{\cdot}058$. F. p. of treated solvent, 9·837° c.):							
0·01413	0·331°	0·342°	0·339°	0·337°	6·06	5·98	5·87
0·02850	0·669	0·688	0·684	0·678	6·05	5·95	5·83
0·04231	1·000	1·027	1·021	1·015	6·10	5·98	5·86
0·07391	1·762	1·808	1·799	1·790	6·18	6·01	5·87
0·08450	2·023	2·075	2·062	2·052	6·21	6·04	5·88
0·1083	2·598	2·665	2·647	2·635	6·24	6·03	5·85

The calculation of accurate ν-factors involves taking account of the already noted fact that water does not behave as an infinitely strong base in sulphuric acid, with the result that the water used to suppress the self-dissociation of the solvent has its own degree of ionisation altered by the added inorganic sulphate. Thus the depression of freezing point which follows the addition of the sulphate is smaller than it would have been if the effect of the pre-treatment water on the freezing point had remained constant. In order to correct for this, it is necessary to know the basicity constant for water $K_b(H_2O) = [H_3O^+][HSO_4^-]/[H_2O]$.

FIG. 4.

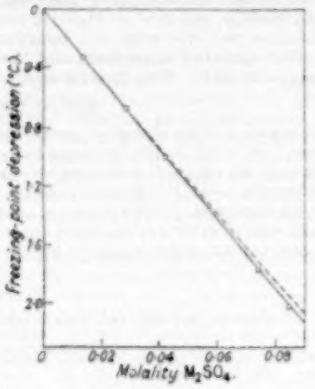
Depression of the freezing point of water-treated sulphuric acid by potassium sulphate.



○ *Expt.* 86. ◐ *Expt.* 63. ◔ *Expt.* 85.
– – – – *Calc. for* $k_f = 5{\cdot}98$ *deg. g.-mol.*$^{-1}$ *kg., neglecting solvation* (n = 0).
——— *Ditto, allowing for solvation* (n = 2).

FIG. 5.

Depression of the freezing point of water-treated sulphuric acid by ammonium sulphate.



○ *Expt.* 123.
– – – – *Calc. for* $k_f = 5{\cdot}98$ *deg. g.-mol.*$^{-1}$ *kg., neglecting solvation* (n = 0).
——— *Ditto, allowing for solvation* (n = 1).

In Part II, the effect of added water on the freezing point of sulphuric acid is studied, and some values of K_b are deduced. They are not very accurate, depending as they do on the manner in which corrections are applied for residual, unrepressed self-dissociation, and for solvation of the ionic dissociation products. But a value deduced by a given procedure will accurately reproduce the experimental results, if it is applied in association with the same procedure. In the case now under discussion, the most convenient way of computing the part played by the water in modifying the freezing-point depression arising from the addition of the ionising sulphates is to use the value $K_b(H_2O) = 0{\cdot}72$ g.-mol. kg.$^{-1}$. This requires that we omit any explicit correction for residual self-dissociation, but allow for solvation of the hydroxonium ion with solvation number unity.

Employing the formula $0{\cdot}72 = \{(\nu - 1)^2 m_2 + (\nu - 1)m'\}/(2 - \nu)$, we first compute a ν-factor for water in molality m_2, in the presence of a molality m' of hydrogen sulphate ions derived from the added potassium or ammonium sulphate. Then, from the ν-factor, we calculate the freezing-point depression due to the water, by means of the appropriate form of equation (4), in applying which water is regarded as the experimental solute A, whilst the potassium or ammonium sulphate is taken as the solute B. We substitute $s_2 = 2$ and $\nu_2 = 2$, for the reason explained in connexion with the derivation of equation (5); and, assuming each formed ion-pair, potassium hydrogen sulphate or ammonium hydrogen sulphate, to be solvated with n molecules of sulphuric acid, according to equations of some such form as

$$K_2SO_4 + (2n + 1)H_2SO_4 = 2K(H_2SO_4)_n^+ + 2HSO_4^-$$

we make the further substitutions $s_2 = 2n + 1$ and $\nu_2 = 4$, thus obtaining the specialised equation

$$\Delta\theta = 5{\cdot}98\{m_2[1 - 0{\cdot}0036\bar{\theta}] + (2\overline{m_2} + (2n + 1)m_2/10{\cdot}20)\}$$

Here $\Delta\theta$ is the depression of freezing point due to the water, m_1 is the molality of the water, and m_2 is that of the potassium or ammonium sulphate. Since at this stage a correction term only is being calculated, it is sufficient to insert, as has been done, the provisional value of the cryoscopic constant, 5·98 deg. g.-mol.$^{-1}$ kg., which was derived in Section 2.2. The determination of the solvation number n is discussed below. By employing this equation, first with an experimental value of the sulphate molality m_2, and then with m_2 set equal to zero, one obtains two values of $\Delta\theta$, the difference between which is the correction sought. This has to be added to the observed depression of freezing point due to the sulphate, in order to correct for the changed behaviour of the pre-treatment water. Having thus obtained corrected depressions of freezing point due to the sulphate, one may now compute values of k_f by means of equation (5), in which $\Delta\theta$, $\bar{\theta}$, Δm_2, and $\overline{m_2}$ all now refer to potassium or ammonium sulphate, and m_2 refers to the pre-treatment water. Therefore we have to insert $z_2 = 2n + 1$ and $\nu_2 = 4$, thus obtaining the following specialised form :

$$\Delta\theta/\Delta m_2 = 4k_f[1 - 0{\cdot}0035\bar{\theta} + \{4(2n - 1)\overline{m_2} + (2n + 1)m_2\}/20{\cdot}40]$$

We may direct attention first to the results of calculations in which solvation of the inorganic sulphate is neglected, so that n is set equal to zero. In Table VII one sees (cf. especially Expt. 86, in which Δm_2 is varied over a 10-fold range) that the calculated values under the heading $k_f(n = 0)$ are fairly steady at the lower values of Δm_2, but rise markedly at the higher values (the same is shown by Expts. 63 and 85, taken together). The direction of this non-ideality in the more concentrated solutions is not that which might indicate an effect of inter-ionic attraction. It is the direction which points to solvation of one or both of the formed ions as the source of the disturbance; and we shall try in this way to account for the effect. In principle this is easily done : we have only to insert the appropriate value of the solvation number n into the equations already given. The best criterion for n is the constancy of k_f over a range of concentrations of the solute. As Table VII shows, the condition of constancy is best satisfied by the value $n = 2$. Hence we conclude that the solvation number for potassium hydrogen sulphate is approximately 2, and that the mean value of k_f, calculated with this solvation number, is the result which we should accept as the value of the cryoscopic constant given by this group of experiments. It appears that the solvation number of ammonium hydrogen sulphate is appreciably less than that of the potassium salt. This is confirmed in the experiments next to be mentioned; and a survey of all our results has led to the conclusion that, for the ammonium salt, the nearest integral value is $n = 1$.

In our second procedure for dealing with sulphates, sulphuric acid of maximal freezing point was taken as solvent, and the first added portions of the experimental solutes were trusted to generate hydrogen sulphate ions in sufficient quantity largely to suppress their production from sulphuric acid. In this case, the residual, unrepressed production of hydrogen sulphate ions from the solvent was computed, and the appropriate allowances were made. It was assumed that dissociation processes which do not involve hydrogen sulphate ions remain unaltered by the added solute. Some results, obtained by this method for the solutes potassium and ammonium sulphate, are recorded in Tables IX and X.

TABLE IX.

Freezing points of solutions of potassium sulphate in anhydrous sulphuric acid.

K_2SO_4 (Δm_2).	F. p. (° c.).	Depressions. $\Delta\theta_1$.	Depressions. $\Delta\theta_2$.	k_f (deg. g.-mol.$^{-1}$ kg.). $n = 0$.	$n = 1$.	$n = 2$.
Expt. 122 (F. p. of solvent, 10·357° c.) :						
0·00579	10·278	0·242°	—	—	—	—
0·01205	10·165	0·355	0·287°	5·96	5·95	5·94
0·03653	9·620	0·900	0·872	5·99	5·96	5·93
0·05618	9·154	1·366	1·348	6·04	5·99	5·94
0·07080	8·795	1·725	1·711	6·09	6·02	5·95
0·08243	8·504	2·016	2·004	6·13	6·05	5·97
0·1268	7·374	3·146	3·137	6·24	6·11	5·98
Expt. 121 (F. p. of solvent, 10·352° c.) :						
0·01548	10·091	0·429°	0·372°	6·02	6·00	5·98
0·02509	9·852	0·638	0·600	6·00	5·97	5·94
0·04779	9·354	1·166	1·145	6·03	5·98	5·93
0·06224	9·003	1·517	1·501	6·08	6·01	5·94
0·07967	8·576	1·944	1·932	6·13	6·03	5·93

TABLE X.

Freezing points of solutions of ammonium sulphate in anhydrous sulphuric acid.

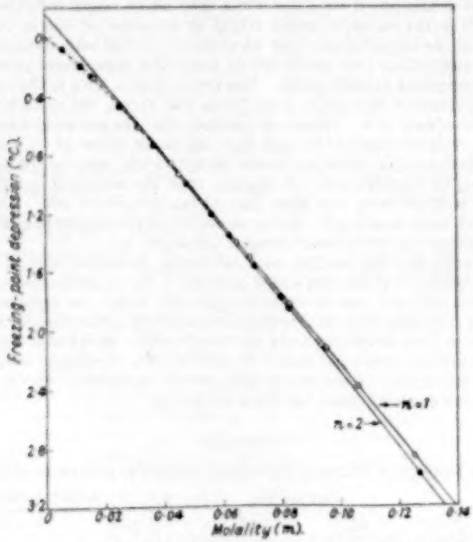
Am_2SO_4 (Δm_2).	F. p. (° c.).	Depressions. $\Delta\theta_1$.	Depressions. $\Delta\theta_2$.	k_f.* $n = 0$.	k_f.* $n = 1$.	Am_2SO_4 (Δm_2).	F. p. (° c.).	Depressions. $\Delta\theta_1$.	Depressions. $\Delta\theta_2$.	k_f.* $n = 0$.	k_f.* $n = 1$.
Expt. 110 (F. p. of solvent, 10·353° c.):						*Expt.* 111 (F. p. of solvent, 10·350° c.):					
0·04240	9·492	1·028°	1·004°	5·95	5·92	0·01625	10·077	0·436°	0·382°	5·98	5·96
0·06931	8·851	1·669	1·654	6·01	5·95	0·03140	9·739	0·776	0·746	6·00	5·97
0·08266	8·530	1·999	1·978	6·04	5·95	0·04516	9·420	1·095	1·073	6·00	5·95
0·09490	8·229	2·291	2·281	6·09	5·97	0·06465	8·933	1·562	1·547	6·06	5·98
0·1058	7·963	2·557	2·547	6·10	5·97						
0·1259	7·489	3·031	3·023	6·14	5·98						

* In deg. g.-mol.$^{-1}$ kg.

In calculating the results of these experiments, one has not to deal with the variable degree of ionisation of water, and this permits some simplification of procedure. After enough salt has been added largely to suppress the production from sulphuric acid of hydrogen sulphate ions, the freezing-point curve runs very nearly linearly over a wide range of solute concentrations. So slight is the curvature that the graph may be produced back, as is shown in Fig. 6, to locate

FIG. 6.

Depression of the freezing point of anhydrous sulphuric acid by potassium sulphate and by ammonium sulphate.



● *Experimental points for potassium sulphate* (*Expts.* 121, 122).
○ " " *ammonium* " (*Expts.* 110, 111).
—— *Theoretical curves, allowing for solvation of the solutes.*
- - - - *Curve showing the disturbance of solvent ionisation.*

with considerable precision, on the axis of zero solute concentration, a point which represents what the freezing point of sulphuric acid would be in the absence of that form of dissociation which generates hydrogen sulphate ions. The extrapolation can equally be made with the help of theoretical equations for freezing-point depression. The extrapolated freezing point lies at 10·52° c.* The depressions tabulated under the heading $\Delta\theta_1$ are reckoned from this

* In Parts IV and V the temperature 10·52° c. is obtained again in several different ways: it seems to be closely located. It must not be confused with the temperature 10·62° c. deduced in Part II for the freezing point of sulphuric acid in the absence of *all* forms of dissociation.

temperature. In general, a part of this depression will be caused by the products of that form of solvent dissociation which gives hydrogen sulphate ions, *viz.*, the autoprotolytic reaction

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

Much of this dissociation process may have been suppressed by the introduced hydrogen sulphate ions, but a part will survive. How much survives can be calculated with the help of the ionic product

$$K_{ap} = [H_3SO_4^+][HSO_4^-] = 1{\cdot}7 \times 10^{-4} \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

the determination of which is described in Part IV. From the concentration of added hydrogen sulphate ions, the concentration of surviving sulphuric acidium ions can thus be deduced; and from this, the partial depression of freezing point caused by un-repressed autoprotolysis may be derived by means of the formula $\delta\theta = 11{\cdot}96[H_3SO_4^+]$. By subtraction, $\Delta\theta_2 = \Delta\theta_1 - \delta\theta$, we obtain the corrected depressions, θ_2, due to the added solute only. From θ_2, we have now to compute k_f by means of the appropriate specialisation of equation (5), *viz.*,

$$\Delta\theta'/\Delta m_2 = 4k_f(1 - 0{\cdot}0035\bar{\theta} + (4n - 2)\overline{m}_2/10{\cdot}20)$$

where θ is the difference between the real freezing point, 10·36°, of sulphuric acid and the mean between the extrapolated freezing point, 10·52°, and the observed freezing point of the solution.

In the above formula, n represents, as before, the solvation number of potassium or ammonium hydrogen sulphate. We have already concluded that the solvation numbers of potassium and ammonium hydrogen sulphate are approximately 2 and 1, respectively: these values are now confirmed, using the criterion of the constancy of the derived k_f values. The latter we take to be the values, which are indicated by the present group of experiments, for the cryoscopic constant of sulphuric acid.

We summarise in Table XI the values of the cryoscopic constant (k_f, in units deg. g.-mol.$^{-1}$ kg.) which follow from these experiments on the depression of the freezing point of water-treated, and of anhydrous, sulphuric acid by the solutes potassium and ammonium sulphate. Theoretical curves of freezing-point depression, calculated from the equations already given, with the use therein of the cryoscopic constant 5·97 deg. g.-mol.$^{-1}$ kg., are shown in Figs. 4, 5, and 6. Evidently, they well represent the observational data.

TABLE XI.

Determination of the cryoscopic constant k_f *(deg. g.-mol.*$^{-1}$ *kg.) of sulphuric acid.*

(Method 2.)

Solute.	Expt. no.	Solute molality.	Water molality.	k_f.	Solute.	Expt. no.	Solute molality.	Water molality.	k_f.
K_2SO_4	88	0·01—0·08	0·047	5·97	Am_2SO_4	123	0·02—0·11	0·058	6·00
	86	0·02—0·05	0·048	5·96		110	0·04—0·03	0·001	5·96
	89	0·03—0·08	0·056	5·96		111	0·04—0·06	0·002	5·97
	122	0·06—0·13	0·000	5·95					
	121	0·03—0·08	0·001	5·95					
			Mean	5·97					

(2.4) *Cryoscopic Evaluation of the Constant (Third Method).*—The conclusion that electrostatic activity effects are negligible in dilute solution in sulphuric acid allows us, subject to certain limitations, to employ organic bases for the determination of the cryoscopic constant. The limitations are that the bases shall be completely ionised according to the general equation

$$B + H_2SO_4 = BH^+ + HSO_4^-,$$

that they shall have no basic centre other than the one responsible for this reaction, and that they shall not react with the solvent in any other way than as bases. We have found a number of quite differently constituted organic bases which fulfil these conditions. They all give essentially the same final result, as we shall here illustrate with the solutes acetone and acetic acid, leaving the other cases for record, and for discussion on different lines, in later parts of the series.

The experimental results are given in Tables XII and XIII. The observed depressions of freezing point are represented graphically in Fig. 7, from which it will be seen that the depressions given by the two solutes define a common curve.

According to the chemical equation given above, the measured depressions of freezing point will be due in part to hydrogen sulphate ions; and therefore we have to employ sulphuric acid solvents in which the self-dissociation of the sulphuric acid has been suppressed. The suppres-

sion was secured by pre-treatment with water. This necessitated correcting the observed depressions of freezing point, just as is described in Section 2.3, for that change in the degree of ionisation of the water which results from the generation of hydrogen sulphate ions by the added organic base. From the corrected depressions, the cryoscopic constant, k_f, was calculated by means of equation (5), with the substitutions, $z_3 = 1$ and $\nu_3 = 2$, as required by the above-written chemical equation. These calculations were made at first without regard to possible solvation of the ions of the organic oxonium hydrogen sulphate.

TABLE XII.

Freezing points of solutions of acetone in sulphuric acid.

Me_2CO (Δm_3).	$\Delta\theta$. (uncorr.).	$\Delta\theta$ (corr.). $n = 0.$	$n = 1.$	$n = 2.$	k_f (deg. g.-mol.$^{-1}$ kg.). $n = 0.$	$n = 1.$	$n = 2.$
Expt. 92 (molality H_2O, $m_1 = 0{\cdot}045$. F. p. of treated solvent, 10·016° c.):							
0·0169	0·200°	0·205°	0·204°	0·203°	6·05	5·98	5·92
0·0282	0·337	0·346	0·343	0·342	6·12	6·02	5·95
0·0476	0·565	0·578	0·575	0·572	6·05	5·97	5·88
0·0671	0·799	0·816	0·812	0·808	6·07	5·97	5·87
0·0864	1·028	1·050	1·045	1·040	6·08	5·97	5·84
0·1158	1·383	1·411	1·405	1·398	6·09	5·96	5·84

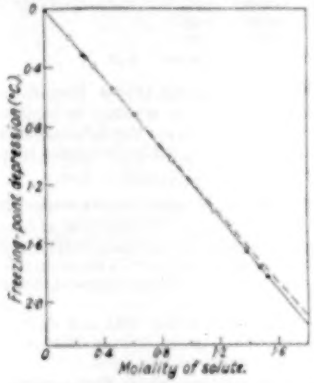
TABLE XIII.

Freezing points of solutions of acetic acid in sulphuric acid.

$Me{\cdot}CO_2H$ (Δm_3).	$\Delta\theta$ (uncorr.).	$\Delta\theta$ (corr.). $n = 0.$	$n = 1.$	$n = 2.$	k_f (deg. g.-mol.$^{-1}$ kg.). $n = 0.$	$n = 1.$	$n = 2.$
Expt. 89 (molality H_2O, $m_1 = 0{\cdot}050$. F. p. of treated solvent, 9·977° c.):							
0·0332	0·397°	0·407°	0·404°	0·402°	6·09	6·01	5·93
0·0462	0·553	0·566	0·563	0·560	6·11	6·02	5·93
0·0609	0·721	0·737	0·733	0·730	6·03	5·94	5·83
0·1166	1·388	1·416	0·410	1·403	6·06	5·94	5·81
0·1533	1·828	1·864	1·856	1·847	6·09	5·94	5·79
Expt. 88 (molality H_2O, $m_1 = 0{\cdot}063$. F. p. of treated solvent, 9·851° c.):							
0·0261	0·311	0·320	0·318	0·317	6·10	6·01	5·94
0·0731	0·872	0·895	0·890	0·885	6·11	5·99	5·87
0·1142	1·346	1·380	1·372	1·364	6·08	5·94	5·79
0·1390	1·632	1·692	1·683	1·673	6·10	5·94	5·78
0·1479	1·762	1·804	1·794	1·784	6·11	5·95	5·78

FIG. 7.

Depression of the freezing point of sulphuric acid by acetone and by acetic acid.



○ *Acetone (Expt. 92).* ◑ *Acetic acid (Expt. 89).* ◒ *Acetic acid (Expt. 88).*
– – – – *Calc. for* $k_f = 5{\cdot}98$ *deg. g.-mol.*$^{-1}$ *kg., neglecting solvation of the solute* (n = 0).
——— *Ditto, allowing for solvation* (n = 1).

The more general treatment of the data takes account of the possibility that either or both of the ions of the organic oxonium hydrogen sulphate may be solvated with a total of s molecules of solvent. The chemical equation for the ionisation of the organic base then takes some such form as the following:

$$B + (s + 1)H_2SO_4 = BH(H_2SO_4)_s^+ + HSO_4^-$$

Accordingly we have to employ equation (5) with the substitutions $s = s + 1$ and $\nu_2 = 2$, where s is not necessarily zero. These calculations have been made for a number of values of s, and the results are given in Tables XII and XIII. Using the criterion of the constancy of k_f, it follows that the investigated range of s-values, 0—2, contains the true solvation number, the best round value of which is 1. The mean k_f values, obtained on this basis from the results of the different experiments, are summarised in Table XIV.

TABLE XIV.

Determination of the cryoscopic constant (k_f) of sulphuric acid.

Method 3.

Solute (and range of its molality).	Expt. no.	Molality of water.	k_f (deg. g.-mol.$^{-1}$ kg.).
Acetone ($0 < m < 0{\cdot}12$)	92	0·045	5·98
Acetic acid ($0 < m < 0{\cdot}16$)	89	0·050	5·96
	88	0·063	5·96
		Mean	5·97

Employing the mean value $k_f = 5{\cdot}97$ deg. g.-mol.$^{-1}$ kg., theoretical curves of freezing-point depressions for basic solutes, such as acetone and acetic acid, have been computed assuming the solvation numbers 0 and 1. These are shown in Fig. 7, together with the experimental points for acetone and acetic acid.

(2.5) *Values of the Cryoscopic Constant.*—In the preceding sections, three groups of experiments have been reported, through which we have sought to determine the cryoscopic constant of sulphuric acid. They give closely concordant results, which are noted in Table XV.

TABLE XV.

Cryoscopically determined values of the cryoscopic constant of sulphuric acid.

Method.	Section.	Types of solute.	Examples.	k_f (deg. g.-mol.$^{-1}$ kg.).
(1)	2.2	Non-electrolytes	SO_2Cl_2, $Cl{\cdot}SO_3H$	5·98
(2)	2.3	Salts	K_2SO_4, $(NH_4)_2SO_4$	5·97
(3)	2.4	Bases	Me_2CO, $Me{\cdot}CO_2H$	5·97

Because of the more direct nature of the procedure involved in applying method (1), we weight its result more highly than those of the other two methods; but the latter furnish useful confirmation. Accordingly, we have adopted the value

$$k_f = 5{\cdot}98 \text{ deg. g.-mol.}^{-1} \text{ kg.}$$

as the uniform basis of the calculations reported in the accompanying papers of this series.

(3) *The Heat of Fusion of Sulphuric Acid.*

It is considered that the figure $k_f = 5{\cdot}98$ deg. g.-mol.$^{-1}$ kg. is more nearly correct than any previously derived value for the cryoscopic constant of sulphuric acid. Therefore we have used this figure for the purpose of computing a value for the heat of fusion of sulphuric acid, hoping that the value so derived will be more nearly correct than any of the values which have been determined calorimetrically. Employing the formula $\Delta H_s^f = RT_s^2/k_f m_1$, and the numerical data $R = 1{\cdot}9866$ cal. deg.$^{-1}$ g.-mol.$^{-1}$, $T_s = 10{\cdot}36°$ C. $= 283{\cdot}5°$ K., $k_f = 5{\cdot}98$ deg. g.-mol.$^{-1}$ kg., and $m_1 = 10{\cdot}196$ g.-mol. kg.$^{-1}$, we obtain for the molar heat of fusion $\Delta H_s^f = 2605$ cal. g.-mol.$^{-1}$.

(4) *The Freezing Point of Sulphuric Acid.*

It has been mentioned that the only practicable way of preparing sulphuric acid free from an excess of either sulphur trioxide or water is to adjust its composition, by the addition of one or other of these solutes, until the freezing point reaches a maximum. This has been done on numerous occasions with many samples of sulphuric acid; and always the freezing-point

maximum has been found to lie between 10·35° and 10·36°. The readings have usually lain in the range 10·356° ± 0·002°, but the standardisation of our temperatures on the international scale of temperature cannot be guaranteed to the last of these figures, and our value for the freezing point is therefore quoted as 10·36° ± 0·01° c.

This result seems very surprising, because most of the previously recorded values lie higher. The following freezing points of sulphuric acid have been recorded :

Marignac (*Ann. Chim. Phys.*, 1853, **39**, 184)	10·6° c.
Pickering (*Proc. Roy. Soc.*, 1891, **49**, 11)	10·35
Pictet (*Compt. rend.*, 1894, **119**, 642)	10·5
Knietsch (*Ber.*, 1901, **34**, 4100)	10·0
Bredig (*Z. Elektrochem.*, 1906, **12**, 460)	10·43
Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257)	10·46
Oddo and Scandola (*Gazzetta*, 1908, **38**, i, 603)	10·43
Lichty (*J. Amer. Chem. Soc.*, 1908, **70**, 1934)	10·43
Brönsted (*loc. cit.*)	10·49
Robles and Moles (*loc. cit.*)	10·52
Rubin (*cf.* Yost and Russell, *op. cit.*)	10·31
This investigation	10·36

We made many attempts to raise our value of the maximal freezing point. Our usual method of preparing sulphuric acid for cryoscopic experiments consisted of distilling a small excess of sulphur trioxide from oleum into 98% " AnalaR " sulphuric acid, at room temperature and at low pressure, in all-glass apparatus, and then adjusting the freezing point of the resulting acid by successive small additions of distilled water. The analytically determinable impurities in the " AnalaR " acid can have had no detectable effect upon the observed freezing points. We tried to improve the treatment of this acid in several ways. One way was separately to condense the sulphur trioxide obtained from the oleum, and to redistil it, before passing it into the 98% acid. In case any small amount of sulphur dioxide present in the oleum had passed through into the sulphuric acid, this was heated at 200° at a low pressure until practically all the excess of sulphur trioxide had been removed. In another attempt to eliminate any disturbance due to sulphur dioxide, potassium perdisulphate was added to the oleum from which the sulphur trioxide was distilled. None of these modifications of procedure made any difference to the observed maximal freezing points. Therefore, finally, the sulphuric acid was subject to repeated fractional freezing, the bulk of retained material being thus reduced to less than one-tenth of the original bulk. Even this treatment failed to yield an acid with a higher maximal freezing point, and therefore we cannot help concluding that the freezing point of sulphuric acid is 10·36°.

It is difficult to account adequately for the differences between this result and those given in the literature. No doubt the temperatures recorded by the early workers were on the mercury-thermometer scale, and therefore require correction to bring them to the international temperature scale. At 10° c. the correction amounts to −0·05°, and thus accounts for a part of the discrepancy. The remainder must be assumed to be due to general thermometric errors. These remarks do not, one imagines, apply to the recent determination by Rubin ; here our assumption is that thermometry was accurate, but that his acid contained an excess of either sulphur trioxide or water.

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498. *Cryoscopic Measurements in Sulphuric Acid. Part II. The Solutes Water and Sulphur Trioxide. The Basic Strength of Water, and the Acid Strength of Disulphuric Acid.**

By R. J. Gillespie.

The freezing point of the system water–sulphur trioxide has been studied at compositions in the neighbourhood of that of sulphuric acid. The results and conclusions differ somewhat from those of earlier investigators. From data applying to the water side of the freezing-point maximum at sulphuric acid, it is deduced that the ionisation of water as a base in solvent sulphuric acid is appreciably incomplete; a basicity constant for water is derived. From the results applying to the sulphur trioxide side of the freezing-point maximum, it is concluded that disulphuric acid* is moderately ionised; a value for its acidity constant is computed, which, however, is provisional, and is to be improved in Part IV, where account will be taken of effects, here neglected, due to the higher polysulphuric acids. From the degree of rounding of the freezing-point maximum, a value is derived for the total concentration in which solutes are formed by the self-dissociation of sulphuric acid.

(1) *Methods and Results.*

(1.1) *Objects and Background.*—Of fundamental importance for the understanding of the properties of solvent sulphuric acid is a knowledge of the behaviour of the solutes water and sulphur trioxide. The reason is partly that the study of these solutes is the first step in an investigation designed to elucidate the self-ionisation of the solvent; and it is partly that so many of the solutes, with whose condition in solvent sulphuric acid we shall be concerned in the following papers, furnish water, amongst other substances, or at least the products into which, in these conditions, water is converted.

The effect of the solutes water and sulphur trioxide on the freezing point of sulphuric acid has been investigated by Pickering (*J.*, 1890, **57**, 365), by Knietsch (*Ber.*, 1901, **34**, 4069), by Giran (*Compt. rend.*, 1913, **157**, 221), and by Hulsmann and Biltz (*Z. anorg. Chem.*, 1934, **218**, 373), but only at compositions so widely spaced that it is not possible to derive from the results any precise conclusions concerning the conditions of the solutes in dilute solution. More intensive investigations of the freezing points of dilute solutions of these solutes in sulphuric acid are recorded by Hantzsch (*Z. physikal. Chem.*, 1908, **62**, 243), by Oddo and Scandola (*Gazzetta*, 1908, **38**, 603), by Robles and Moles (*Anal. Fis. Quim.*, 1936, **34**, 331), and by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900).

(1.2) *Method.*—A detailed reinvestigation of the freezing point of the water–sulphur trioxide system for compositions in the neighbourhood of that of pure sulphuric acid, *i.e.*, of the cryoscopic behaviour of the solutes water and sulphur trioxide in dilute solution, has now been undertaken. The results and conclusions differ somewhat from those obtained by earlier workers.

The method was to follow the change in freezing point produced by adding successive, small, weighed amounts of water to a known weight of sulphuric acid containing initially a small excess of sulphur trioxide. The freezing points were measured as is described in Part I (preceding paper). The precise amount of sulphur trioxide in the initial acid was not known at the commencement of an experiment, but after the freezing-point measurements had been made, all compositions could be calculated from the weights, with the aid of the assumption that the composition at the freezing-point maximum is that of pure sulphuric acid.

(1.3) *Results.*—The data obtained in several such experiments are given in Table I. Compositions are expressed in molalities for theoretical convenience. On the water side of the freezing-point maximum they are in molalities of water, but on the sulphur trioxide side they are given, not in molalities of sulphur trioxide, but in molalities of disulphuric acid,* the assumption having been made that the solute sulphur trioxide is converted substantially entirely in dilute solution into disulphuric acid. Of course, the distinction of composition is only that a small proportion of the total sulphuric acid counts as belonging to the solvent in one case, but not in the other; and thus the differences are numerically small, though not inappreciable.

* The acid $H_2S_4O_7$, usually called pyrosulphuric acid, is here termed disulphuric acid, because this name belongs to a scheme of nomenclature which can conveniently be extended to the acids $H_2S_3O_{10}$ (trisulphuric acid) and $H_2S_4O_{13}$ (tetrasulphuric acid), the presence of which in oleum is cryoscopically demonstrated in Part IV of this series, and is spectroscopically confirmed in an accompanying paper (Millen); and a salt of the acid $H_2S_5O_{16}$ is described in another of the accompanying papers (Goddard, Hughes, and Ingold). The preferred nomenclature agrees with the established names of analogous acids of other elements of Group VI of the Periodic Table, *e.g.*, the polychromic, polymolybdic, and polytungstic acids.

TABLE I.

Freezing points of solutions of water and disulphuric acid in sulphuric acid.

Weights (g.). Added H_2O.	Soln.	Solute.	H_2SO_4.	Molality of solute.	F. p. (° c.).
Expt. No. 26 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	126·07	7·084	118·99	0·3345	8·071
0·1344	126·20	5·754	120·45	0·2685	8·532
0·1311	126·33	4·458	121·87	0·2061	8·951
0·0580	126·39	3·885	122·51	0·1782	9·163
0·0751	126·47	3·144	123·33	0·1431	9·412
0·0974	126·57	2·179	124·39	0·0979	9·748
0·0654	126·64	1·533	125·11	0·0686	9·957
0·0643	126·70	0·939	125·86	0·0400	10·153
0·0315	126·73	0·628	126·10	0·0260	10·243
		H_2O.		H_2O.	
0·0635	126·79	0·0045	126·79	0·0020	10·351
0·0317	126·81	0·0362	126·79	0·0160	10·299
Expt. No. 66 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	117·85	2·229	115·62	0·1048	9·694
0·0482	117·90	1·752	116·15	0·0812	9·868
0·0447	117·94	1·357	116·58	0·0598	10·015
0·0449	117·99	0·966	117·12	0·0381	10·160
0·0447	118·04	0·424	117·62	0·0168	10·289
		H_2O.		H_2O.	
0·0429	118·08	0·0074	118·07	0·0035	10·340
0·0436	118·12	0·0436	,,	0·0240	10·224
0·0445	118·17	0·0881	,,	0·0459	10·032
0·0426	118·21	0·1307	,,	0·0651	9·821
0·0450	118·25	0·1857	,,	0·0863	9·585
0·0450	118·30	0·2307	,,	0·1075	9·353
0·0439	118·34	0·2746	,,	0·1283	9·127
0·0452	118·39	0·3198	,,	0·1496	8·878
0·0469	118·44	0·3657	,,	0·1712	8·644
0·0419	118·48	0·4076	,,	0·1909	8·421
Expt. No. 67 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	126·99	2·171	124·82	0·0998	9·727
0·1329	127·12	0·857	126·26	0·0401	10·144
0·0450	127·16	0·412	126·75	0·0203	10·272
0·0417	127·20	0·041	127·15	0·0020	10·350
		H_2O.		H_2O.	
0·0423	127·24	0·0378	127·20	0·0165	10·294
0·0435	127·29	0·0815	,,	0·0355	10·129
0·0452	127·33	0·1265	,,	0·0553	9·928
0·0406	127·37	0·1671	,,	0·0730	9·737
0·0400	127·41	0·2071	,,	0·0905	9·537
0·0433	127·45	0·2504	,,	0·1094	9·330
0·0433	127·49	0·3037	,,	0·1284	9·117
0·0409	127·53	0·3446	,,	0·1462	8·914
0·0426	127·57	0·3872	,,	0·1648	8·710
Expt. No. 73 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	129·27	3·687	125·57	0·1650	9·248
0·1888	129·46	1·830	127·63	0·0805	9·869
0·0649	129·52	1·189	128·33	0·0521	10·064
0·0323	129·56	0·869	128·69	0·0386	10·163
0·0330	129·59	0·546	129·05	0·0238	10·253
0·0345	129·62	0·202	129·42	0·0089	10·330
		H_2O.		H_2O.	
0·0345	129·65	0·0141	129·64	0·0060	10·350
0·0344	129·68	0·0485	,,	0·0207	10·284
0·1119	129·79	0·1304	,,	0·0640	9·855
0·0645	129·85	0·2149	,,	0·0918	9·549
0·0453	129·90	0·2602	,,	0·1112	9·346
0·0670	129·97	0·3272	,,	0·1398	9·013

Weights (g.). Added H_2O.	Soln.	Solute.	H_2SO_4.	Molality of solute.	F. p. (° c.).
Expt. No. 76 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	125·46	1·224	125·31	0·0553	10·066
0·0944	125·55	0·2907	125·56	0·0107	10·327
0·0294	125·58	0·0000	125·58	0·0000	10·352
		H_2O.		H_2O.	
0·0334	125·61	0·0334	125·58	0·0148	10·282
0·0339	125·64	0·0673	,,	0·0298	10·181
0·0670	125·71	0·1343	,,	0·0594	9·875
0·0392	125·79	0·1935	,,	0·0856	9·579
0·0652	125·86	0·2587	,,	0·1145	9·264
0·0644	125·92	0·3231	,,	0·1429	8·943
0·0650	125·98	0·3881	,,	0·1717	8·656
Expt. No. 79 :					
		H_2O.		H_2O.	
—	120·29	0·1150	120·18	0·0532	9·939
0·0367	120·33	0·1517	,,	0·0702	9·778
0·0692	120·40	0·2209	,,	0·1021	9·427
0·0644	120·46	0·2853	,,	0·1319	9·087
0·0682	120·53	0·3535	,,	0·1634	8·732
0·0683	120·60	0·4218	,,	0·1950	8·380
Expt. No. 80 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	125·94	0·447	125·49	0·0200	10·276
0·0314	125·97	0·137	125·83	0·0061	10·337
0·0050	125·98	0·087	125·89	0·0039	10·342
		H_2O.		H_2O.	
0·0325	126·01	0·0237	125·99	0·0105	10·322
0·0327	126·04	0·0564	,,	0·0249	10·219
0·0684	126·11	0·1248	,,	0·0550	9·914
0·0663	126·17	0·1911	,,	0·0842	9·592
Expt. No. 90 :					
		H_2O.		H_2O.	
—	127·03	0·0114	127·04	0·0050	10·343
0·0345	127·08	0·0459	,,	0·0201	10·263
0·0694	127·15	0·1153	,,	0·0504	9·971
0·0686	127·22	0·1839	,,	0·0804	9·645
0·0900	127·31	0·2739	,,	0·1198	9·202
0·0739	127·38	0·3478	,,	0·1521	8·840
0·0680	127·45	0·4158	,,	0·1819	8·513
0·0700	127·52	0·4858	,,	0·2125	8·180
0·0698	127·59	0·5556	,,	0·2430	7·832
Expt. No. 102 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	128·94	6·975	122·01	0·3211	8·180
0·1167	129·00	5·827	123·28	0·2654	8·563
0·2564	129·32	3·720	126·06	0·1473	9·389
0·1326	129·45	2·002	127·49	0·0882	9·809
0·1312	129·58	0·7117	128·91	0·0310	10·210
0·0677	129·65	0·0462	129·60	0·0020	10·346
		H_2O.		H_2O.	
0·0357	129·69	0·0310	129·65	0·0133	10·329
Expt. No. 103 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	130·51	7·140	123·37	0·3253	8·181
0·4678	130·98	2·514	128·47	0·1100	9·668
0·1924	131·17	0·6118	130·56	0·0263	10·239
0·0307	131·20	0·3084	130·89	0·0132	10·307
		H_2O.		H_2O.	
0·0358	131·23	0·0046	131·23	0·0020	10·344

TABLE II.

Freezing points of the water–sulphur trioxide system (Hammett and Deyrup).

Weights (g.).				Molality of solute.	F. p. (° c.).
Added H_2O.	Soln.	Solute.	H_2SO_4.		
Run I :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	53·70	2·906	50·79	0·3155	8·171
0·0737	53·77	2·228	51·54	0·2369	8·766
0·0733	53·84	1·453	52·39	0·1498	9·345
0·0595	53·90	0·884	53·02	0·0877	9·803
		H_2O.		H_2O.	
0·0874	53·99	0·0058	53·99	0·0060	10·350
0·0229	54·01	0·0287	,,	0·0296	10·180
0·0310	54·04	0·0597	,,	0·0615	9·836
0·0232	54·06	0·0849	,,	0·0874	9·532
0·0152	54·08	0·1001	,,	0·1030	9·348
0·0188	54·10	0·1189	,,	0·1224	9·127
0·0320	54·13	0·1509	,,	0·1553	8·717

Weights (g.).				Molality of solute.	F. p. (° c.).
Added H_2O.	Soln.	Solute.	H_2SO_4.		
Run II :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	57·90	2·670	55·17	0·2719	8·485
0·0422	57·94	2·243	55·63	0·2265	8·810
0·0497	57·99	1·751	56·17	0·1751	9·177
0·0425	58·03	1·331	56·63	0·1321	9·482
0·0396	58·07	0·940	57·06	0·0925	9·772
0·0183	58·09	0·758	57·26	0·0744	9·905
0·0311	58·12	0·463	57·59	0·0452	10·125
0·0129	58·13	0·324	57·73	0·0315	10·220
0·0074	58·14	0·250	57·82	0·0230	10·275
0·0077	58·15	0·174	57·90	0·0164	10·315
0·0088	58·16	0·087	58·00	0·0084	10·339
		H_2O.		H_2O.	
0·0161	58·17	0·0073	58·16	0·0070	10·342
0·0158	58·19	0·0231	,,	0·0221	10·239
0·0177	58·21	0·0408	,,	0·0390	10·062
0·0941	58·30	0·1349	,,	0·1288	9·013

(1.4) *Results of Hammett and Deyrup.*—It will be necessary to compare Hammett and Deyrup's results (*loc. cit.*) for the freezing point of the water–sulphur trioxide system with those now recorded. For this purpose a recalculated version of Hammett and Deyrup's freezing-point data is presented in Table II. Here, as in Table I, compositions are expressed as molalities of water, or of disulphuric acid. Hammett and Deyrup did not record Celsius temperatures, but only readings on a Beckmann thermometer; and therefore, in order to facilitate comparison with the present results, it has been assumed that the temperature at the maximum of their freezing-point curves was 10·35° c. in every case; and all their temperature readings have been brought to this scale.

Over the range of composition with which this investigation deals, the freezing-point curve for the water–sulphur trioxide system consists of two nearly linear portions with a rounded maximum in between. This is shown in Fig. 1. The following discussion will largely be concerned with what can be learned from the slopes and exact shapes of the nearly linear portions, and from the amount of rounding of the maximum.

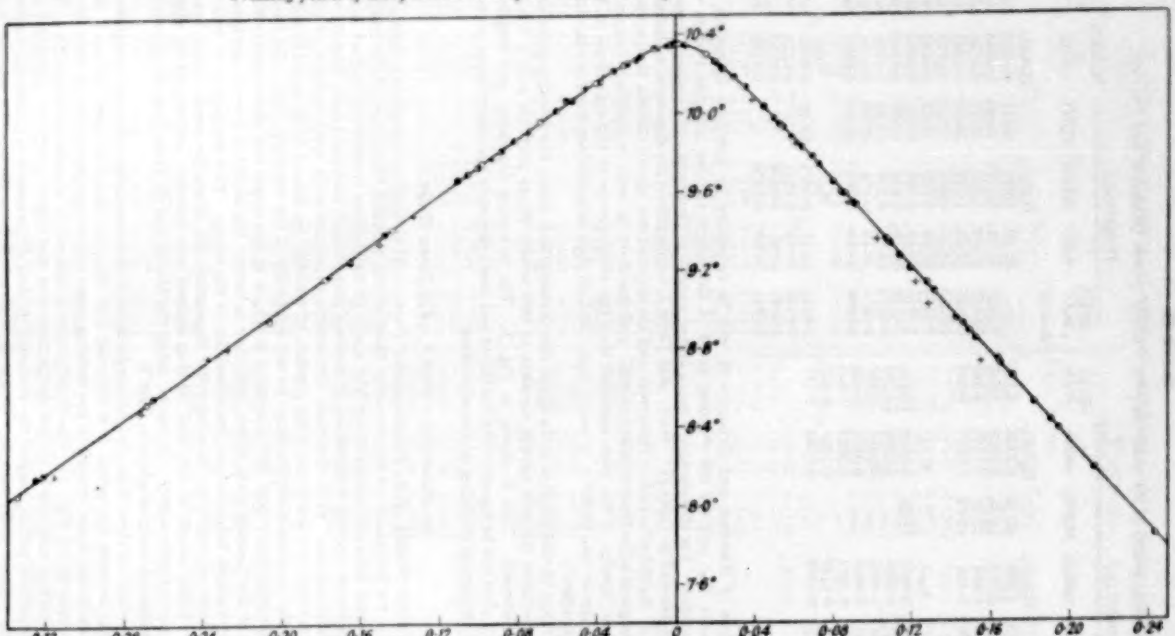
(2) *Discussion. Part I. The Solute Water.*

(2.1) *The Water Branch of the Freezing-point Curve.*—At concentrations greater than about 0·05 molal, *i.e.*, for compositions not too near those of the rounded maximum of the freezing-point curve, water behaves qualitatively like many of the solutes considered in Part I—like acetone, for instance—giving depressions of freezing point which increase nearly linearly with the solute concentration. It is therefore convenient to regard each total content of solute water as divided into two portions. One portion, of molality m_s (about 0·05), is considered to be present for the purpose of suppressing the self-ionisation of the sulphuric acid. Its effect is to bring the freezing point from the maximum down on to the upper end of the nearly linear water-branch of the freezing-point curve, and thus to render the modified solvent suitable for study of the cryoscopic behaviour of the remainder of the water. This remainder, of molality Δm_s, now produces an additional freezing-point depression, $\Delta\theta$, down the nearly linear branch of the curve. From values of Δm_s and $\Delta\theta$ thus defined and selected, one should be able to calculate an approximate ν-factor for water, using the theoretical formula, and the cryoscopic constant for sulphuric acid, as given in Part I.

We shall proceed on these lines, but before doing so it is necessary to note that a significant difference exists between the values now reported and those of Hammett and Deyrup: their results would make the water branch of the freezing-point curve slope more steeply than do the present measurements (cf. Fig. 1). The discrepancy is difficult to explain satisfactorily. The direction and relative magnitude of the deviations, and the slight scatter of Hammett and Deyrup's experimental points, suggest the intrusion in their experiments of a little adventitious water with each weighed water sample. Of course, such an explanation leaves a sense of doubt,

FIG. 1.

Freezing points of the system water–sulphur trioxide at compositions near that of sulphuric acid.



and therefore the present determinations of the water branch of the freezing-point curve were independently repeated a considerable number of times (more than are fully reported here) in the hope of eliminating the discrepancy. This proved impossible: the results of the experiments were so accurately consistent that one is compelled to accept them.

(2.2) *The Incomplete Ionisation of Water.*—The general nature of the conclusion to which these results lead can be seen without calculation. If we measure the average slope of the nearly linear water branch of the freezing-point curve, as determined in this investigation, we find that it is 11·21 deg. g.-mol.$^{-1}$ kg. This figure has to be compared with the cryoscopic constant of sulphuric acid, 5·98 deg. g.-mol.$^{-1}$ kg. (cf. Part I). The error which, in this simple form of comparison, arises from the lack of exact linearity of the water-branch is less than 1%. It will be evident that, if we should assume that water is completely ionised in solvent sulphuric acid according to the equation

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

then the ν-factor for water would be exactly 2, and the average slope of the water-branch would be 2 × 5·98 = 11·96 deg. g.-mol.$^{-1}$ kg., to within 1%. The observed slope falls short of this by 6%. The difference cannot be due to electrostatic activity effects, for it was shown in Part I by a comparison of non-electrolytic and electrolytic solutions (cf. *J.*, 1950, 2485 *et seq.*) that electrostatic effects are quite inappreciable in sulphuric acid solutions over the range of concentrations with which we are here concerned. The effect of solvation may not be inappreciable, but its direction is such as to widen the discrepancy. Thus it would seem necessary to conclude that water is not completely ionised in sulphuric acid.

Both Hantzsch, and Hammett and Deyrup, concluded from their cryoscopic measurements that water is almost completely ionised in sulphuric acid and they made no further comment on the matter. Hantzsch's data were, of course, not sufficiently precise to justify a consideration of somewhat small deviations. Hammett and Deyrup obtained a larger experimental slope for the water-branch of the freezing-point curve than that now found. Their slope amounted to 11·85 deg. g.-mol.$^{-1}$ kg., and, in conjunction with our cryoscopic constant, 5·98 deg. g.-mol.$^{-1}$ kg., this would mean nearly complete ionisation. But Hammett and Deyrup were using the substantially higher value, 6·15 deg. g.-mol.$^{-1}$ kg., for the cryoscopic constant, and the deviation of their measured slope from twice this value might well have suggested incomplete ionisation. However, the conclusion that water is practically completely ionised as a base in sulphuric acid was accepted by them, and seems to have been accepted quite generally.

TABLE III.

ν-Factors for solute water in solvent sulphuric acid.

Expt. no.	Molality of water. m_2.	Δm_2.	F. p. (° c.).	ν-Factor.
66	0·0651	—	9·821	—
	,,	0·0212	9·585	1·87
	,,	0·0424	9·353	1·81
	,,	0·0632	9·127	1·85
	,,	0·0845	8·878	1·87
	,,	0·1061	8·644	1·87
	,,	0·1258	8·421	1·87
			Mean	1·86
67	0·0730	—	9·737	—
	,,	0·0175	9·537	1·92
	,,	0·0364	9·330	1·85
	,,	0·0554	9·117	1·88
	,,	0·0732	8·914	1·89
	,,	0·0918	8·710	1·88
			Mean	1·88
76	0·0594	—	9·875	—
	,,	0·0262	9·579	1·89
	,,	0·0551	9·264	1·86
	,,	0·0836	8·943	1·88
	,,	0·1124	8·656	1·83
			Mean	1·87
79	0·0702	—	9·778	—
	,,	0·0319	9·427	1·85
	,,	0·0617	9·087	1·88
	,,	0·0932	8·732	1·88
	,,	0·1248	8·380	1·89
			Mean	1·88
90	0·0804	—	9·645	—
	,,	0·0394	9·202	1·89
	,,	0·0717	8·840	1·89
	,,	0·1015	8·513	1·88
	,,	0·1321	8·170	1·89
	,,	0·1626	7·832	1·89
			Mean	1·89

(2.3) *Approximate ν-Factors for Water.*—The average number of kinetically separate, dissolved particles (molecules or ions) which are formed in consequence of the addition of one molecule of water to the solution—the ν-factor for water—may be calculated, by the methods set forth in Part I, from observations along the nearly linear water-branch of the freezing-point

curve. As a first approximation, we may employ equation (4) of Part I, substituting $z_1 = z_2 = 1$ and $\nu_1 = \nu_2 = 2$, and thus reducing the equation to the simple form written below, in which the determined value of the cryoscopic constant has been inserted :

$$\Delta\theta/\Delta m_2 = 5{\cdot}98\nu_2(1 - 0{\cdot}0035\bar{\theta}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The mean depression $\bar{\theta}$ has, of course, to be reckoned with reference to the freezing point of pure sulphuric acid. Some values of ν for water, calculated in this way, are given in Table III. They lead to the mean value $\nu = 1{\cdot}89$.

The above method of calculating ν-factors is probably not the best available for two reasons. In Part I evidence was adduced for the view that potassium and ammonium hydrogen sulphates are solvated in sulphuric acid. In Part III (*J.*, 1950, paper no. 499) it will be shown that nitronium and nitrosonium hydrogen sulphates behave similarly to the potassium and ammonium salts in this respect. It seems probable that most ionic compounds, not excluding hydroxonium hydrogen sulphate, are solvated in sulphuric acid. In Section 2.6 of this paper a qualitative argument is given which suggests that the non-ionised water molecule is solvated in sulphuric acid. Confirming these assumptions, it is shown in Section 2.5 that, in the calculation of the basicity constant for water, an improvement in consistency results, if the assumption is made that both water and the ion-pair which it forms are solvated with a solvation number of about unity. The reaction of water with the sulphuric acid solvent may therefore be represented by some such equation as the following :

$$H_2O + 2H_2SO_4 \rightleftharpoons H_2O(H_2SO_4) + H_2SO_4 \rightleftharpoons H_2O(H_2SO_4)^+ + HSO_4^-$$

Accordingly, the ν-factors should be calculated by specialising equation (4) of Part I by the substitutions $z_1 = z_2 = 2$ and $\nu_1 = \nu_2 = 2$.

The conclusion that water is incompletely ionised in sulphuric acid evidently entails the consequence that the ν-factor should in principle *not* be constant and equal to 1·88 : it should rise towards 2·00 with increasing dilution. The reason why this is not apparent in Table III is that the calculations are not sufficiently accurate, and the range of water concentrations is too limited. Nevertheless theory shows that, apart from causes of curvature of which our equations take account, the nearly linear water branch of the freezing-point curve should be additionally curved, steepening from the observed slope of 11·21 deg. g.-mol.$^{-1}$ kg. to the theoretical limiting slope of 11·96 deg. g.-mol^{-1} kg. as the freezing point of pure sulphuric acid is approached. We cannot observe this because another disturbance intervenes : the slope falls to zero, owing to the self-ionisation of sulphuric acid. It will be necessary to give further consideration to this disturbance also before attempting to treat the incomplete ionisation of water more quantitatively.

(2.4) *The (Theoretical) Freezing Point of Non-dissociated Sulphuric Acid.*—It is generally accepted that the rounding of the freezing-point maximum is due to the self-ionisation of sulphuric acid. This might be a simple proton transfer :

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

However, in Part IV (*J.*, 1950, paper no. 500) reasons will be given for believing that it is more complex, involving also a sulphur trioxide transfer, thus,

$$2H_2SO_4 \rightleftharpoons H_2S_2O_7 + H_2O$$

together with the ionisation of the formed disulphuric acid and water, approximately in accordance with the following equations :

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$
$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

The hydrogen sulphate ion is a product of both forms of self-ionisation, and the hydroxonium ion is a product of the second form; wherefore the addition of water, which produces both these ions, will repress both forms of self-ionisation, and the resulting disappearance of ions will diminish the initial effect of added water in depressing the freezing point. Again, the sulphuric acidium ion arises in both forms of self-ionisation, and the hydrogen disulphate ion arises in the second form; and, since these are the ions of disulphuric acid, added sulphur trioxide will act qualitatively like added water; and thus we should find rounding on both sides of the freezing-point maximum, as, indeed, we do.

In order to be able to compute the degree of ionisation of water as a function of its concentration, we require to know what the freezing point of sulphuric acid would be in the

absence of any self-ionisation. This temperature cannot be estimated by merely producing backwards the nearly linear branches of the freezing-point curve, so that they meet in a point above the rounded maximum; for, as we have seen in the case of the water branch—and a quite similar argument applies to the sulphur trioxide branch—these nearly linear branches are not linear; in particular, they would steepen materially, if it were not for the disturbances of self-ionisation, at compositions close to that of sulphuric acid. Therefore it is necessary to find, by trial calculations, that value of the theoretical freezing point which gives the most consistent results on applying it to the computation of the degree of ionisation of water. The value finally chosen, 10·62°, is probably not in error by more than 0·02°.*

(2.5) *The Basic Strength of Water in Sulphuric Acid.*—By calculating freezing-point depressions as differences between the theoretical freezing point of non-dissociated sulphuric acid and the observed freezing points of solutions of water in sulphuric acid, over the solute concentration range 0·05—0·25 molal, it is possible to compute the equilibrium constant

$$K_b(H_2O) = [H_3O^+][HSO_4^-]/[H_2O]$$

Two steps are involved. Writing $\Delta\theta'$ for the freezing-point depression calculated from the theoretical freezing point, and $\Delta m = m_s + \Delta m_b$ for the *total* molality of solute water, a ν-factor is first computed from the equation

$$\Delta\theta'/\Delta m = 5{\cdot}98\,\nu\,(1 + 0{\cdot}0035\,\bar{\theta}') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(cf. equation 1, p. 2498). Here $\bar{\theta}'$ is to be obtained by subtracting, from the real freezing point of sulphuric acid, 10·36°, the mean between the freezing point of the solution and the theoretical freezing point of non-dissociated sulphuric acid, 10·62°. Having thus found ν, the basic ionisation constant is computed from the mass-law equation

$$K_b(H_2O) = (\nu - 1)^2 m/(2 - \nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This procedure neglects two disturbances. The first arises from incompleteness in the suppression, by the added water, of the self-dissociation of the solvent. This can be computed from the values, given in Part IV, of the equilibrium constants of the two main dissociation processes of sulphuric acid, *viz.*,

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$
$$K_w = [H_3SO_4^+][HSO_4^-] = 1{\cdot}7 \times 10^{-4}\ \text{g.-mol.}^2\ \text{kg.}^{-2}$$
$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$$
$$K_d = [H_3O^+][HS_2O_7^-] = 0{\cdot}7 \times 10^{-4}\ \text{g.-mol.}^2\ \text{kg.}^{-2}$$

In calculating the residual self-dissociation, we take the added water as completely converted into H_3O^+ and HSO_4^-. Having from the above constants computed $[H_3SO_4^+]$ and $[HS_2O_7^-]$, we employ the formula $\delta\theta = 11{\cdot}96([H_3SO_4^+] + [HS_2O_7^-])$, which gives, with sufficient approximation, the freezing-point depression $\delta\theta$ due to the surviving self-dissociation. This must be subtracted from $\Delta\theta'$ to give $\Delta\theta'' = \Delta\theta' - \delta\theta$.

There remains the disturbance caused by solvation. In order to take it into account, it is necessary to calculate ν-factors, neither with equation (2), nor with this equation with $\Delta\theta''$ written for $\Delta\theta'$, but by means of an equation for $\Delta\theta''/\Delta m$, which is derived from equation (4) of Part I by writing $s_2 = s_3 = n + 1$ and $\nu_2 = \nu_3 = 2$ in the nearly unit correction factor. Here n is the solvation number of hydroxonium hydrogen sulphate. The equation is

$$\Delta\theta''/\Delta m = 5{\cdot}98\nu\,(1 - 0{\cdot}0035\bar{\theta}'' + 2n\bar{m}/10{\cdot}20) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the ν-factors derived from it have to be inserted into equation (3) for the purpose of computing $K_b(H_2O)$.

The method employed for the evaluation of the solvation number n is so to choose it that the most nearly constant values of K_b result. Unfortunately, there is a large percentage error in the determination of K_b, because, as equation (3) shows, the value derived depends fundamentally on the small quantity $2 - \nu$, that is, on the experimental determination of the small difference between the actual slope of the water branch of the freezing-point curve and the slope it would have if the ionisation of water were as complete as has hitherto been thought. For this reason the solvation number cannot be determined at all exactly. However, the

* The freezing point, 10·62°, in the absence of all forms of dissociation, is to be distinguished from the freezing-point, 10·52°, in the absence only of the autoprotolysis (cf. Part I, *J.*, 1950, 2488).

calculations have been made with various trial values, $n = 0$, 1, 2, etc., and $n = 1$, which gives moderately consistent K_b values, has been selected as the best round figure.

The upper part of Table IV contains two of the sets of K_b values which have been computed for experiment No. 90. One set (headed $n = 0$) is derived by neglecting solvation. The other (headed $n = 1$) is computed with the inclusion of a correction for solvation, the solvation number being taken as unity. The lower part of Table IV contains a summary of the mean K_b values calculated from all the experiments, with the same allowance for solvation. From the overall mean, $K_b = 1{\cdot}2$ g.-mol. kg.$^{-1}$, it can be computed that, at 0·1 molal concentration, about 7% of water remains non-ionised in solvent sulphuric acid.

TABLE IV.

Basic ionisation constant of water in sulphuric acid (Expt. 90).

Molality, H_2O (*m*).	F. p. (° c.).	Depression. $\Delta\theta'$.	$\Delta\theta''$.	ν-Factors. $n = 0$.	$n = 1$.	$K_b(H_2O)$. $n = 0$.	$n = 1$.
0·0504	9·971	0·649°	0·596°	1·98	1·97	—	—
0·0804	9·645	0·975	0·940	1·96	1·94	1·9	1·2
0·1198	9·202	1·418	1·395	1·95	1·93	2·2	1·5
0·1521	8·840	1·780	1·758	1·94	1·91	2·2	1·5
0·1819	8·513	2·147	2·089	1·93	1·90	2·3	1·5
0·2125	8·170	2·480	2·436	1·93	1·89	2·6	1·6
0·2430	7·872	2·788	2·777	1·92	1·87	2·6	1·5

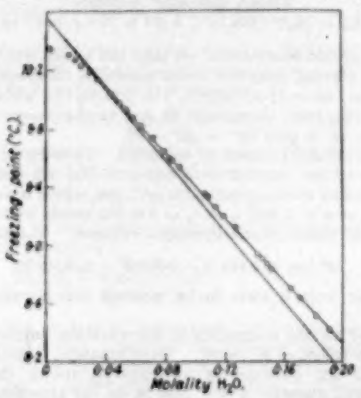
Summary of basicity constants (calc. with $n = 1$):

Expt. No.	66	67	76	79	90	Mean
$K_b(H_2O)$	1·1	1·1	1·3	1·1	1·4	1·2 g.-mol. kg.$^{-1}$.

The value of K_b is somewhat uncertain, because it is very sensitive to the error of experiment and of the applied corrections. If we neglect solvation, the mean value of K_b becomes 1·8 g.-mol. kg.$^{-1}$. If we retain the correction for solvation, but neglect the residual solvent dissociation, then the derived value is 0·72 g.-mol. kg.$^{-1}$. For the purpose of reproducing experimental results by calculation, it matters little which value is taken provided the computing

FIG. 2.

Theoretical freezing-point curves for solute water in solvent sulphuric acid.



procedure corresponds to the value assumed. In Fig. 2 a theoretical freezing-point curve for water is shown, which is computed from the last-mentioned value; and it is compared with the experimental points. The upper part of the diagram shows the effect on the freezing point of the repression by the added water of the self-ionisation of sulphuric acid. The lower curve is calculated from equation (3) by taking ν as constant and equal to 2.

(2.6) *Remarks on the Basicity of Water in Sulphuric Acid.*—The conclusion that water is incompletely ionised in sulphuric acid whilst, as was shown in Part I, acetic acid and acetone are fully ionised in this solvent, seems to invite comment. When water, acetic acid, and acetone are acting as solvents for acids, *e.g.*, for the hydrogen halides, water is definitely more basic than either acetic acid or acetone. Yet when these three substances have the role of solutes in solvent sulphuric acid, water is less basic than either of the other two. This illustrates the recognised impossibility of setting up an absolute table of acid-strengths or base-strengths; and it shows that specific molecular interactions between solute and solvent play a part, which can be at least as important as are differences of proton affinity, in the determination of acid–base equilibria.

As to the reason for the small basicity of water in sulphuric acid, the obvious line of thought is that the relatively considerable thermodynamic stability of non-ionised water in solvent sulphuric acid is to be ascribed to solvation; and, more particularly, to the ability of a water molecule to occupy the place of a sulphuric acid molecule in the closely-knit hydrogen-bonded structure of liquid sulphuric acid (cf. Part I), and to do this without disrupting the surrounding liquid structure. The non-ionised forms of the solutes acetone and acetic acid will, because of the size of these molecules, and the lack of affinity of their hydrocarbon portions for sulphuric acid, cause a considerable disruption of the surrounding sulphuric acid structure. They will be rendered by this much less stable relatively to their ionised forms.

(3) *Discussion. Part II. The Solute Sulphur Trioxide.*

(3.1) *The Sulphur Trioxide Branch of the Freezing-point Curve.*—The general form of this branch of the freezing-point curve will be clear from Fig. 1: at compositions sufficiently removed from the rounded maximum, the sulphur trioxide branch becomes nearly linear, but much less sloping than the water branch. The mean slope, according to the present determinations, for a range of concentrations of disulphuric acid from 0·3 molal to 0·05 molal, is 7·40 deg. g.-mol.$^{-1}$ kg. Obviously disulphuric acid is yielding many fewer ions than water produces.

Hantzsch concluded from his cryoscopic measurements that disulphuric acid was almost completely non-ionised in sulphuric acid. He found, however, that these dilute oleum solutions have quite a high electrical conductivity. He therefore assumed that disulphuric acid is a very weak acid, but that the hydrogen ion in sulphuric acid possesses an unusually high mobility.

Hammett and Deyrup record the value 7·55 deg. g.-mol.$^{-1}$ kg. for the slope of the nearly linear part of the sulphur trioxide branch of the freezing-point curve. Their conclusion was either that disulphuric acid was a weak electrolyte, or that it undergoes a complex ionisation involving the polymerisation of sulphur trioxide.

The simplest explanation of the fact that sulphur trioxide gives a curve of freezing-point depressions having a slope intermediate between those appropriate to a non-electrolyte and a binary electrolyte is that, in dilute solution in sulphuric acid, solute sulphur trioxide is converted almost completely into disulphuric acid, which is ionised as a weak acid according to the equation:

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-$$

Actually this assumption is too simple. For it will be shown in Part IV (*J.*, 1950, paper no. 800) that solutions of sulphur trioxide in sulphuric acid contain, besides disulphuric acid, appreciable amounts of higher polysulphuric acids. However, for the present we shall, for simplicity, neglect the disturbance caused by these higher acids, although the estimates which we shall thus derive of the degree of ionisation of disulphuric acid will be only provisional and will be shown in Part IV to require a significant correction.

It should be remarked that the conclusion that sulphur trioxide is converted in dilute solution mainly into disulphuric acid does not follow from the cryoscopic results; as far as they are concerned, the distinction between sulphur trioxide and non-ionised disulphuric acid molecules is only slight, one being merely a monosolvated form of the other. But the fact that, on increasing the concentration of sulphur trioxide until a new solid phase appears, the new phase is, not sulphur trioxide, but disulphuric acid, shows that, even in such relatively high concentration, solute sulphur trioxide is converted largely into disulphuric acid; and it is a fair assumption that this conversion will be much more nearly complete in the dilute solutions relevant to this work. In principle, the cryoscopic results will measure (*a*) the concentration of the ions of disulphuric acid, and (*b*) the concentration of the non-ionised disulphuric acid

molecules *plus* any free sulphur trioxide. The concentration of free sulphur trioxide is expected to bear a small constant proportion to the concentration of non-ionised molecules of disulphuric acid. It is difficult to say whether or not this small proportion is completely negligible, but if it is not, then these small concentrations of sulphur trioxide must be held to be included in the stated concentrations of non-ionised disulphuric acid.

(3.2) *The Acid Strength of Disulphuric Acid in Solvent Sulphuric Acid.*—It has been mentioned that the average slope of the nearly linear part of the sulphur trioxide branch of the freezing-point curve is 7·40 deg. g.-mol.$^{-1}$ kg. But, as already illustrated in the example of the solute water, this figure has no simple and exact molecular significance; for not only is the nearly linear curve in fact non-linear, but also it is theoretically expected to be non-linear for various reasons, of which the most important relates to the different proportions in which disulphuric acid should be ionised at different dilutions, according to Ostwald's law. This effect should cause the curve to steepen, from slopes in the neighbourhood of 7·40 deg. g.-mol.$^{-1}$ kg. to a limiting slope of 11·96 deg. g.-mol.$^{-1}$ kg., as the composition of pure sulphuric acid is approached. One does not observe this, because the self-ionisation of the solvent causes the gradient actually to fall away at compositions near that of sulphuric acid. Indeed, over a considerable band of concentrations, the two effects, one tending to steepen the curve and the other tending to slacken its gradient, nearly cancel each other, producing a deceptive near-linearity and a slope which is meaningless from a molecular point of view.

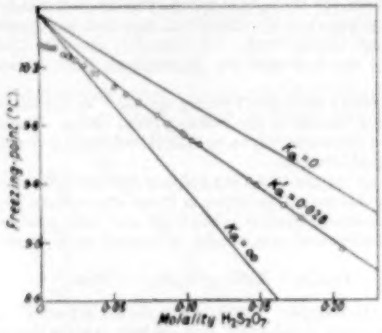
The procedure for calculating ν, and hence the equilibrium constant

$$K_a(H_2S_2O_7) = [H_2SO_4^+][HS_2O_7^-]/[H_2S_2O_7]$$

is similar to that illustrated for the solute water. Using the theoretical freezing point of the non-dissociated solvent, we compute ν, as a function of concentration, by means of an appropriate form of the general equation, employing for the purpose observations of freezing point in the

FIG. 3.

Theoretical freezing-point curves for the solute disulphuric acid in solvent sulphuric acid.



region of concentration 0·08—0·35 molal disulphuric acid. The equation used is derived from equation (4) of Part I by inserting the approximate figure $\nu_s = 1·3$ into the nearly unit correction factor, and by substituting also $s_s = \nu_s - 1 = 0·3$, as is required for the reaction

$$H_2S_2O_7 + H_2SO_4 = H_2SO_4^+ + HS_2O_7^-$$

(since $m_s = 0$, values for s_s and ν_s are not required). The resulting equation is

$$\Delta\theta'/\Delta m = 5·98\nu\,(1 - 0·0035\bar{\theta}' - 0·7\bar{m}/10·20) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

where Δm is the total molarity of disulphuric acid, $\Delta\theta'$ is the depression of freezing point, reckoned with reference to the theoretical freezing point, $\bar{m}$ is the mean molality over the finite interval, and $\bar{\theta}'$ is the mean depression computed as stated on p. 2499. The ν-factors thus obtained are now improved as follows. From them, the approximate concentrations $[H_2SO_4^+]$ and $[HS_2O_7^-]$ are derived. From these, and the already mentioned ionic products K_{ap} and K_{id}, we compute

the small concentrations of surviving HSO_4^- and H_3O^+ and thence the partial depressions, $\delta\theta = 11{\cdot}96([HSO_4^-] + [H_3O^+])$, caused by residual self-dissociation. These partial depressions are now applied as corrections, $\Delta\theta'' = \Delta\theta' - \delta\theta$, and equation (5) is used again, but with $\Delta\theta''$ replacing $\Delta\theta'$. The final step is to compute the equilibrium constant $K_a(H_2S_2O_7)$ by means of the mass-law equation

$$K_a(H_2S_2O_7) = (\nu - 1)^2 m/(2 - \nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Some values of K_a, thus deduced from two experiments, are given in Table V.

TABLE V.

Acid ionisation constant of disulphuric acid in sulphuric acid.

Molality of $H_2S_2O_7$.	F. p. (° c.).	Depression. $\Delta\theta'$.	$\Delta\theta''$.	ν ($m = 0$).	$K_a(H_2S_2O_7)$.
Expt. No. 26 :					
0·0079	9·748	0·872°	0·802°	1·38	0·023
0·1431	9·412	1·210	1·158	1·36	0·029
0·1782	9·163	1·457	1·411	1·34	0·031
0·2061	8·951	1·669	1·627	1·33	0·033
0·2685	8·532	2·088	2·052	1·30	0·035
0·3345	8·071	2·549	2·519	1·28	0·036
Expt. No. 102 :					
0·0882	9·809	0·811	0·743	1·42	0·027
0·1473	9·389	1·231	1·177	1·35	0·028
0·2054	8·563	2·057	2·019	1·29	0·031
0·3211	8·180	2·440	2·406	1·27	0·032

From these figures, and similar computations based on other experiments, one may deduce a mean value of the acid dissociation constant of disulphuric acid in sulphuric acid, *viz.*, $K_a(H_2S_2O_7) = 0{\cdot}028$ g.-mol. kg.$^{-1}$. Disulphuric acid in sulphuric acid is thus a *somewhat* weak acid (like oxalic acid in water).

Using the above value, a theoretical freezing-point curve for the solute sulphur trioxide has been constructed, just as was done for the solute water. This curve (labelled $K_a' = 0{\cdot}028$) is compared with the experimental data in Fig. 3. The other curves in Fig. 3 (labelled $K_a = 0$ and $K_a = \infty$) are the theoretical curves for disulphuric acid, considered as a non-electrolyte and as a strong electrolyte, *i.e.*, they are the curves for which ν has the values 1 and 2, respectively.

The value 0·028 g.-mol. kg.$^{-1}$ here derived for the acid dissociation constant of disulphuric acid in sulphuric acid will be termed the ***apparent*** dissociation constant of disulphuric acid, and it will be designated $K_a'(H_2S_2O_7)$, as is done in Fig. 3. This is because the value has been computed without making an allowance (for which we have as yet no method) for the formation and ionisation of the higher polysulphuric acids. It will be shown in Part IV that the effect of the formation of these higher poly-acids is not negligible, and that, on this account, the apparent acidity constant of disulphuric acid is substantially larger than the true value.

(4) *Discussion. Part III. Self-dissociation of Sulphuric Acid.*

An important datum for the study of the dissociation of sulphuric acid follows from the results reported here. This datum is the total concentration of all the solute species which arise by the self-dissociation of pure sulphuric acid. Its value may be obtained from the difference between the calculated freezing-point of undissociated sulphuric acid and the maximum observed freezing-point of real sulphuric acid. The difference is $10{\cdot}62° - 10{\cdot}36° = 0{\cdot}26°$, and it corresponds to the total solute concentration 0·043 molal. Assuming the dissociation products to be entirely ionic, the total concentration of uni-univalent electrolytes is thus 0·0215 molal. The problem of the determination of the individual products of the self-dissociation is considered further in Part IV.

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499. *Cryoscopic Measurements in Sulphuric Acid. Part III. The Solutes Nitric Acid, Dinitrogen Pentoxide, Dinitrogen Tetroxide, and Dinitrogen Trioxide. Cryoscopic Proof of the Formation of the Nitronium Ion,* NO_2^+.

By R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold, and E. R. A. Peeling.

It is shown by study of the freezing points that the solutes named in the title react with solvent sulphuric acid according to the following equations:

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$
$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + H_3O^+ + 3HSO_4^-$$
$$N_2O_4 + 3H_2SO_4 = NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$
$$N_2O_3 + 3H_2SO_4 = 2NO^+ + H_3O^+ + 3HSO_4^-$$

These conversions are quantitative, except that, since water is only a semi-strong base (Part II), the ions formed partly recombine:

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

For this reason, the ν-factor of nitric acid is less than 4; the observed value is 3·77, expressed as a mean over the concentrations used. Similarly, the ν-factors for the three oxides are less than 6; the observed mean values are 5·70, 5·69, and 5·69 for the pentoxide, tetroxide, and trioxide, respectively. The deviations from integral values, which are to be expected on account of the incomplete ionisation of water, can be calculated from the basicity constant of water (Part II). The theoretical ν-factors thus computed agree closely with the experimental values.

As is mentioned in Part I, the investigations described in the present paper and in Part V were actually the first to be undertaken of those which are reported in this series. As soon as the kinetic study of aromatic nitration (cf. Hughes, Ingold, and Reed, *J.*, 1950, 2400) had disclosed a rate-determining bond-fission of nitric acid, presumably to form the nitronium ion, it was realised that much of the early work, including all the cryoscopic work, on the condition of nitric acid in solvent sulphuric acid would have to be revised. Such revision in its several aspects was taken in hand; and the cryoscopic experiments quickly solved the problem to which they were directed, namely, that of ascertaining, simply and unambiguously, the products into which nitric acid is converted in sulphuric acid. Soon afterwards, the same kind of information was obtained in the same way for dinitrogen pentoxide, dinitrogen tetroxide, and dinitrogen trioxide.

This work has already been reported in summary (*Nature*, 1946, **158**, 480), but the details have not been published until now for the following reason. At the time of the preliminary report, the cryoscopic results could not be interpreted in a satisfactorily quantitative manner for lack of sufficiently exact information about the general solvent properties of sulphuric acid. The best theory and basic data which were available at that time left differences of several units per cent. between the calculated and observed freezing-point depressions, such differences, although of an order often regarded as negligible, being considerably larger than the experimental error. They could be, and were provisionally, set down to non-ideality; but they could not be proved to be due to that cause, much less accounted for quantitatively on those lines. It followed that a quantitative investigation of the general solvent properties of sulphuric acid would have to be undertaken before the cryoscopic results of special interest to us could be interpreted satisfactorily. That investigation, which has only recently been completed, is described in three of the accompanying papers (Parts I, II, and IV); it provides the required basis for the reduction of our cryoscopic data on nitric acid and the three nitrogen oxides.

(I) *The Solute Nitric Acid.*

(1.1) *Theories of the Condition of Nitric Acid in Sulphuric Acid.*—It has been evident for many years that nitric acid in solution in sulphuric acid exists in an altered form, and that this consists of or contains cations. Saposchnikow's measurements of the partial vapour pressure of nitric acid in water–sulphuric acid mixtures show that, whilst it is large in approximately equimolar solvent mixtures, it becomes relatively small as the solvent composition approaches that of pure sulphuric acid, just as it becomes small when the solvent is nearly pure water (*Z. physikal. Chem.*, 1904, **49**, 697; 1905, **51**, 607; **53**, 225). Hantzsch observed that nitric acid depressed the freezing point of solvent sulphuric acid from two to four times as much as would a solute which dissolved without any form of change (*ibid.*, 1907, **61**, 257; 1908, **65**, 41). These are clear indications that some change occurs. Both Saposchnikow and Hantzsch observed

that solutions of nitric acid in sulphuric acid have a high electrical conductivity (*loc. cit.*), a result which proves that the change gives rise to ions.

The evidence for an altered form of nitric acid in sulphuric acid has been strengthened by later observations on other physical properties of the solutions. Hantzsch observed that solutions of nitric acid in sulphuric acid show little optical absorption in the near ultra-violet, and, in particular, that they show much less absorption than they would if any substantial proportion of the nitric acid were present either as nitric acid molecules or as nitrate ions (*Ber.*, 1925, **58**, 941). Chédin observed that solutions of nitric acid in a sufficient excess of sulphuric acid showed none of the normal Raman spectrum of molecular nitric acid, but instead gave, superposed on the sulphuric acid spectrum, a new and simple spectrum consisting of two strong lines (*Compt. rend.*, 1935, **200**, 1397).

The case for assuming that the altered form of nitric acid in sulphuric acid is cationic rests in part on Hantzsch's proof that nitric acid can, in some conditions, exist in a cationic form. He prepared solid salts from nitric acid and perchloric acid (*Ber.*, 1925, **58**, 941). His conclusions about their compositions and constitutions were quite erroneous (cf. *J.*, 1950, paper no. 505); but he and Berger showed that, when these preparations were electrolysed in solution in nitromethane, nitric acid accumulated at the cathode. It was an obviously probable suggestion that similar salts would be present in solutions of nitric acid in sulphuric acid. Attempts to demonstrate that, in the electrolysis of such solutions, nitric acid is transported towards the cathode have met with difficulties; but such transport has recently been demonstrated for solutions of nitric acid in oleum by Bennett, Brand, and Williams (*J.*, 1946, 875).

Many of the above-mentioned observations are revised or extended in this paper and in accompanying papers. The revision allows much more definite conclusions to be drawn. Our special concern here is with the revision of the cryoscopic evidence, by which we unequivocally identify the altered form of nitric acid as the nitronium ion, NO_2^+.

Throughout the earlier history of the matter, gifted speculation ran ahead of observation and deduction. The three earliest theories about the form assumed by nitric acid in sulphuric acid were all correct or nearly so. Markownikow suggested that it was the mixed anhydride, $NO_2{\cdot}O{\cdot}SO_2H$ (*Ber.*, 1899, **32**, 1441); Saposchnikow that it was nitric anhydride, $NO_2{\cdot}O{\cdot}NO_2$ (*Z. physikal. Chem.*, 1904, **49**, 677); and Euler that it was the nitronium ion, NO_2^+ (*Annalen*, 1903, **330**, 280). Each of these ideas has had many adherents. In supporting the nitric anhydride hypothesis, Chédin emphasised that this substance must be present in some modified form. If it is assumed that both of the above anhydrides are ionised, then the three theories become equivalent.

Hantzsch's views developed along different lines. In his experiments on the depression of the freezing point of sulphuric acid by nitric acid, he employed as solute either nitric acid or potassium nitrate, allowing in the latter case for the depression caused by the formed potassium hydrogen sulphate. In one set of experiments by the first method, and three sets by the second, he obtained depressions due to nitric acid, amounting to 2·2—2·5, 1·9—2·6, 3·3—4·0, and 3·8 times the depression to be expected for a non-electrolyte. (The calculations were naturally based on his value for the cryoscopic constant of sulphuric acid; if our value is used, all the figures would be larger by about one-sixth.) His first (1908) conclusions were that ionising complex acids, such as $(OH)_2NO(SO_4H)$ and $(OH)NO(SO_4H)_2$, are formed, and are extensively ionised.

Later (1925), the general views which Hantzsch had developed to the effect that weaker acids can act as bases towards stronger ones, as well as the special evidence he thought he had secured concerning the compositions of the salts obtained by the interaction of nitric and perchloric acid, led him to abandon the idea that nitric acid in sulphuric acid remains combined in any kind of anion, and to assume instead that it passes into cationic forms. In particular, he assumed univalent and bivalent cations to be furnished by the following reactions:

$$HNO_3 + H_2SO_4 = H_2NO_3^+ + HSO_4^-$$
$$HNO_3 + 2H_2SO_4 = H_2NO_3^{++} + 2HSO_4^-$$

Completed reactions according to these equations would lead to freezing-point depressions respectively equal to twice and thrice the depression to be expected for a non-electrolyte. Hantzsch accepted his previous cryoscopic results as broadly indicative of a three-fold depression, and accordingly assumed that the second reaction is the one that takes place principally in excess of sulphuric acid. He did not attempt to account for his cryoscopic results in detail, or to explain why several experiments had given more than three-fold depressions.

Hantzsch's work on the effect of dissolved nitric acid on the freezing point of sulphuric acid

was repeated by Robles and Moles (*Anal. Fis. Quim.*, 1934, **32**, 474). They obtained freezing-point depressions 2·5—3·3 times that to be expected for a non-electrolyte. (This was on the basis of their value of the cryoscopic constant; ours would make the figures about 10% higher.) They regarded their results as confirming Hantzsch's assumption of a three-fold freezing-point depression. It is not necessary to discuss their interpretation.

(1.2) *Cryoscopic Proof of the Conversion of Nitric Acid into the Nitronium Ion.*—The cryoscopic data now reported exclude the idea that either of Hantzsch's cations of nitric acid is present to any appreciable extent in a solution of nitric acid in sulphuric acid. Our figures accord with the view that nitric acid is quantitatively converted into the nitronium ion; and they are not susceptible of any alternative explanation.

The approximate equation for the conversion of nitric acid into the nitronium ion in solvent sulphuric acid is

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

It indicates a ν-factor of 4 for nitric acid. However, the real ν-factor must be less than 4 on account of the partial recombination of hydroxonium and hydrogen sulphate ions in the balanced reaction

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

The equilibrium constant of this reaction, *i.e.*, the basicity constant of water in solvent sulphuric acid, has been determined (Part II), and this allows us to calculate exact ν-factors for nitric acid at given concentrations.

Even before we proceed to a careful calculation, the general nature of the result can be appreciated. In Part II it was shown that the figure 1·89 could be taken as an average value for the ν-factor of water over the range of solute concentration which we usually employ in our cryoscopic measurements. Making allowance for the nitronium hydrogen sulphate which is formed from nitric acid, simultaneously with water and its ions, we may set down the figure 3·88 as a closer upper limit than 4·00 to the ν-factor for nitric acid. The real ν-factor will be less even than this, because the presence of the nitronium hydrogen sulphate will tend to repress the ionisation of the water. We should over-estimate this common-ion effect if we were to assume that the second hydrogen sulphate ion will double the association of the ions of water, and hence the figure 3·78 should represent a lower limit to the average ν-factor. Thus, without calculation, we may estimate the average ν-factor for nitric acid over our usual range of solute concentrations as $3{\cdot}83 \pm 0{\cdot}06$. In our preliminary report (*Nature*, 1946, **158**, 480), we gave the experimental value 3·82, so that there is substantial agreement. Since the date of that report, both the theoretical and experimental figures have been slightly changed as a result of the use of better procedures for calculation. However, the overall effect of these changes is small, and so the substantial agreement remains. Its confirmation by more careful calculations definitely establishes the explanation expressed in the chemical equations given above.

(1.3) *Calculation of Theoretical ν-Factors for Nitric Acid.*—The principal part of the calculation consists in computing the ν-factor for the water formed in the reaction between nitric acid and the sulphuric acid solvent. This ν-factor, which measures the degree of ionisation of the water, depends on the concentration of the formed water, and on the concentrations of other sources, whether pre-existing or simultaneously produced, of hydrogen sulphate ions. There are two such sources, *viz.*, the water, originally added in order to repress the self-ionisation of the solvent, and the nitronium hydrogen sulphate, which is formed along with water from the nitric acid.

Let us first calculate ν-factors for the total water. Suppose that water in molality m_2 has been added in order to repress the ionisation of sulphuric acid, and that nitric acid in molality m_3 has then been introduced, forming extra water in molality m_2' (with $m_2' = m_3$) and nitronium hydrogen sulphate in molality m_3. Then the basicity constant for water,

$$K_b(H_2O) = [H_3O^+][HSO_4^-]/[H_2O]$$

the concentrations being in molalities, is easily shown to be given by

$$K_b = \{(m_3 + m_2')(\nu_3 - 1)^2 + m_2(\nu_2 - 1)\}/(2 - \nu_3)$$

In Part II, a value of $K_b(H_2O)$ was given, 0·72 g.-mol. kg.$^{-1}$, which is appropriate for calculation by the method here to be used. Employing this figure, ν_3 may be calculated for any given values of m_2 and m_3. Such calculations of the ν-factors for total water in molality $m_2 + m_2'$ are illustrated in columns 1—3 and 7—9 of Table I.

TABLE I.

Theoretical v-factors for water produced from nitric acid in solvent sulphuric acid already containing water.

Molality of added water (m_1).	Molality of added HNO_3 (m_2).	ν_2 for total water.	Depression by total water ($\Delta\theta$).	Depression by water from HNO_3 ($\Delta\theta'$).	ν_2' for water from HNO_3.	Molality of added water (m_1).	Molality of added HNO_3 (m_2).	ν_2 for total water.	Depression by total water ($\Delta\theta$).	Depression by water from HNO_3 ($\Delta\theta'$).	ν_2' for water from HNO_3.
0·050	0·00	1·94	0·583°	—	—	0·065	0·00	1·92	0·751°	—	—
,,	0·02	1·90	0·798	0·215°	1·78	,,	0·02	1·88	0·963	0·212°	1·75
,,	0·04	1·86	1·006	0·423	1·75	,,	0·04	1·85	1·166	0·415	1·72
,,	0·06	1·83	1·211	0·628	1·73	,,	0·06	1·82	1·369	0·618	1·70
,,	0·08	1·80	1·412	0·829	1·71	,,	0·08	1·79	1·566	0·815	1·67
,,	0·10	1·77	1·604	1·021	1·68	,,	0·10	1·76	1·756	1·005	1·65

The next step towards obtaining v-factors for the water formed from nitric acid consists in calculating that part of the depression of the freezing point of the solvent which can be considered to be due to the total water. This requires the use of the appropriate form of equation (4) of Part I. We insert the determined value of the cryoscopic constant; and, in the nearly-unit correction factor, we write, with sufficient accuracy, the values $s_1 = \nu_1 = 2$, and $s_2 = \nu_2 = 0$, thus bringing the equation to the form

$$\Delta\theta = 5{\cdot}98\nu_2(m_2 + m_2')\{1 - 0{\cdot}0035\bar{\theta} + 2(\overline{m_2 + m_2'})/10{\cdot}20\}$$

It is convenient at this stage, and it does not lead to any appreciable error because of the taking of differences later, to set $s_2 = \nu_2 = 0$, thus ignoring the presence and solvation of the nitronium hydrogen sulphate. However, the application of the formula requires care on other counts. For, in the first place, the $\Delta\theta$, which it allows one to compute, represents the partial freezing-point depression, due to total water, below what the freezing point of pure sulphuric acid would be if there were no self-ionisation, *i.e.*, below the " extrapolated " freezing point 10·62° C. (cf. Part II). On the other hand, the mean depression $\bar{\theta}$, as one can understand by considering the physical meaning of the term which contains it, relates to actual not to idealised, freezing points. Therefore, in computing depressions of which $\bar{\theta}$ is the mean, we must first allow for the extra depression, approximately $11{\cdot}96m_2$, caused by the nitronium hydrogen sulphate. Then, having calculated the total depression, due to water plus nitronium hydrogen sulphate, from the extrapolated freezing point, 10·62° C., of the undissociated solvent, we must subtract the temperature corresponding to one-half of this depression from the real freezing point, 10·36° C., of the equilibrium solvent, in order to obtain the mean depression. The numerical work is done by cyclic approximation, a single cycle being sufficient. The computed partial depressions $\Delta\theta$ due to total water are given in the fourth and tenth columns of Table I.

As has been said, these depressions neglect the self-ionisation of the sulphuric acid solvent. However, the water initially introduced in molality m_1 is considered to suppress the solvent dissociation, in conformity with the basis of computation of the employed value of the basicity constant. Therefore, if we subtract the calculated depression, corresponding to the water molality, m_1, from a calculated depression for a larger water molality $m_1 + m_2'$, where $m_2' = m_2$, the difference will represent the real depression $\Delta\theta'$, due to the extra water in molality m_2'; that is, it will represent the partial depression due to water formed from nitric acid in molality m_2. These partial depressions, $\Delta\theta'$, are listed in columns 5 and 11 of Table I.

The corresponding values of ν_2', the v-factors of the water formed from the nitric acid, are given in columns 6 and 12 of Table I. They are readily computed from the depressions, $\Delta\theta'$, by means of the appropriate specialisation

$$\Delta\theta' = 5{\cdot}98\nu_2'm_2'\{1 - 0{\cdot}0035\bar{\theta}' + 2(m_2 + \overline{m_2'})/10{\cdot}20\}$$

of the previously given formula. Here, the mean freezing-point depression, $\bar{\theta}'$, must be reckoned from the true freezing-point of equilibrium sulphuric acid, and must take into account the depressions caused by the nitronium hydrogen sulphate, just as for the previously considered $\bar{\theta}$. But the intervals over which the means $\bar{\theta}'$ are to be taken are different, having, as one limit, the depression given by the originally introduced water.

The theoretical v-factors for nitric acid itself are now obtained by simply adding 2·00 to each of the figures given in columns 6 and 12 of Table I. This addition is made in respect of the formed nitronium hydrogen sulphate.

(1.4) *Experimental ν-Factors for Nitric Acid and their Comparison with the Theoretical ν-Factors.*—The freezing-point depressions produced by nitric acid were measured in solutions in sulphuric acid containing previously introduced water. The added solute was absolute nitric acid, prepared by methods which are standard in this laboratory (Benford and Ingold, *J.*, 1938, 929; Hughes, Ingold, and Reed, *J.*, 1950, 2400).

Supposing the self-ionisation of the sulphuric acid solvent to have been completely suppressed by the initially added water, the ν-factors for nitric acid may be calculated from the further depressions of freezing point produced by the nitric acid, by the use of an appropriate form of equation (5) of Part I. Now it has been established in Parts I and II that potassium, ammonium, and hydroxonium hydrogen sulphates are solvated in sulphuric acid, and it seems inherently probable that the same will be true of nitronium hydrogen sulphate. Such solvation, as well as the solvation of water and its ions, must be taken into account in choosing our specialised equation, which is derived by substituting a suitable value of s_4 in equation (5) of Part I, s_4 being the total number of solvent molecules which, either by reaction or through solvation, are put out of action as solvent, by one molecule of added nitric acid. If n is the solvation number of nitronium hydrogen sulphate, then $s_4 = n + 3$. The only way we have of estimating n is by choosing it to give consistent ν-factors over a range of concentrations. Using this criterion, not only for solute nitric acid (this paper, and Part V), but also for the other investigated solutes which produce nitronium hydrogen sulphate, *viz.*, dinitrogen pentoxide and dinitrogen tetroxide (this paper), and also nitronium perchlorate (Part VI), it is thus estimated that the solvation number n of nitronium hydrogen sulphate lies between 2 and 3, probably nearer to 2. (The sensitivity of the method is insufficient to enable such values to be determined more closely than to the nearest integer.) In order to illustrate the effect of solvation of the nitronium salt, values of ν for nitric acid have been calculated for the n-values 0, 2, and 3, from the experimental freezing-point depressions. The results of these calculations are shown in Table II.

TABLE II.

Depression of the freezing point of sulphuric acid by added nitric acid. Comparison of the experimental and theoretical ν-factors for nitric acid.

Expt. no.	Molality of added H_2O (m_w).	Molality of HNO_3 (Δm_s).	F. p. (° c.).	ν (exptl.). $n = 0$.	$n = 2$.	$n = 3$.	ν (theor.)
2 G •	0·066	—	9·799	—	—	—	—
	,,	0·01463	9·460	3·84	3·79	3·79	3·76
	,,	0·02960	9·109	3·86	3·80	3·79	3·74
	,,	0·04461	8·763	3·84	3·77	3·75	3·72
	,,	0·05946	8·407	3·86	3·78	3·76	3·70
84	0·055	—	9·926	—	—	—	—
	,,	0·00890	9·721	3·84	3·80	3·79	3·78
	,,	0·02213	9·418	3·82	3·77	3·76	3·77
	,,	0·03805	9·061	3·77	3·72	3·70	3·74
	,,	0·06769	8·384	3·82	3·75	3·71	3·72
	,,	0·08231	8·007	3·85	3·77	3·73	3·70

• One of an early series (1942).

The ν-factors computed with allowance for solvation are to be compared with the theoretical ν-factors entered in the last column of the Table. These theoretical factors are calculated from the chemical equations representing the decomposition of nitric acid in sulphuric acid, and the ionisation constant of water, as is illustrated in Section 1.3.

(1.5) *Calculation of a Theoretical Curve for the Freezing-point Depression due to Nitric Acid.*—A theoretical curve for the depression of the freezing point of sulphuric acid by added nitric acid may be calculated by an application of the principles outlined in Sections 1.3 and 1.4. The results of such a calculation are given in Table III. They relate to two cases in which the sulphuric acid solvent has been pre-treated by the addition of water in 0·05 and 0·065 molal concentrations.

Col. 3 in this Table gives the partial depression, calculated for the partly ionised water formed from the nitric acid. These figures are copied from Table I. Col. 4 contains the partial depressions calculated for the binary electrolyte $(NO_2^+)(HSO_4^-)$ into which the nitric acid is assumed to be completely converted, in the presence of the simultaneoutly formed, and previously added water. These figures contain no allowance for the solvation of the nitronium salt; and since, on this basis, one molecule of sulphuric acid is required for the production of one

molecule of the binary electrolyte, equation (5) of Part I is used with the substitutions $s_2 = 1$ and $\nu_2 = 2$, so that it reduces to

$$\Delta\theta/\Delta m_2 = 11{\cdot}06(1 - 0{\cdot}0035\bar{s} + m_2/10{\cdot}20)$$

where m_2 is the total molality of water present. Cols. 5 and 6 give the corresponding partial depressions, as calculated by those special forms of equation (5) of Part I, which take into account the solvation of the nitronium salt with the solvation numbers 2 and 3, so that s_2 becomes 3 and 4, respectively. In all these calculations allowance is made for the presence of the other set of solutes, *viz.*, water and its ions, when computing the mean depression $\bar{\theta}$. The figures in the last three columns of Table III are obtained by addition of the appropriate partial depressions.

TABLE III.

Calculated depressions of the freezing point of sulphuric acid by nitric acid.

Molality of		Freezing-point depressions (° c.):						
			$(NO_2)^+(HSO_4)^-$.			HNO_3.		
added water (m_2).	added HNO_3 (Δm_2).	H_2O and its ions.	$n = 0$.	$n = 2$.	$n = 3$.	$n = 0$.	$n = 2$.	$n = 3$.
0·050	0·02	0·215	0·240	0·245	0·247	0·455	0·460	0·462
,,	0·04	0·423	0·481	0·494	0·500	0·904	0·917	0·923
,,	0·06	0·628	0·723	0·747	0·760	1·351	1·375	1·388
,,	0·08	0·829	0·965	1·005	1·026	1·794	1·834	1·855
,,	0·10	1·021	1·208	1·267	1·297	2·229	2·288	2·319
0·065	0·02	0·212	0·241	0·246	0·248	0·453	0·458	0·460
,,	0·04	0·415	0·482	0·496	0·504	0·897	0·911	0·919
,,	0·06	0·618	0·724	0·751	0·764	1·342	1·369	1·384
,,	0·08	0·815	0·966	1·010	1·031	1·781	1·825	1·846
,,	0·10	1·005	1·209	1·273	1·306	2·214	2·278	2·311

The difference between the depressions for the two different initial water concentrations is very small; and a theoretical freezing-point curve has been constructed from the data for an initial water concentration of 0·05 molal, with a solvation number of 2 for the nitronium hydrogen sulphate. In Fig. 1 (p. 2513), this curve is shown, in comparison with observational points representing the data of Table II. Evidently our theory that nitric acid is converted in sulphuric acid into fully dissociated nitronium hydrogen sulphate and partly ionised water, according to the equations already given, is in satisfactory agreement with experiment.

(2) *The Solute Dinitrogen Pentoxide.*

(2.1) *Theories of the Condition of Dinitrogen Pentoxide in Sulphuric Acid.*—It was noticed by Klemenc and Schöller (*Z. anorg. Chem.*, **1924**, **141**, 231) that solutions of dinitrogen pentoxide in sulphuric acid possess nitrating properties very similar to those of nitric acid in sulphuric acid: not only was nitration by dinitrogen pentoxide a reaction of the second order, like nitration by nitric acid, in solvent sulphuric acid, but also the rates of nitration with these two reagents were practically identical, provided that, in calculating the concentrations, one molecule of dinitrogen pentoxide was taken as the equivalent of two molecules of nitric acid. This would mean, if dinitrogen pentoxide were to dissolve unchanged in sulphuric acid, that the nitric acid is converted into dinitrogen pentoxide, an interpretation which has been suggested or supported more than once. Alternatively, it could mean, if dinitrogen pentoxide is in any way changed in sulphuric acid, that nitric acid is dehydrated and converted into the products of the change.

It was emphasised by Chédin particularly that dinitrogen pentoxide is changed in sulphuric acid. He showed that nitric acid and dinitrogen pentoxide, in solution in sulphuric acid, gave the same Raman spectrum, which was neither that of nitric acid, nor that of dinitrogen pentoxide as this substance exists in non-ionising solvents (in which it had been proved to have a normal molecular weight), but was almost exactly similar to that of the Raman spectrum of solid dinitrogen pentoxide (*Compt. rend.*, **1935**, **200**, 1397; **201**, 724; **1936**, **203**, 722). Therefore Chédin concluded that the substance which was formed from nitric acid, and from dinitrogen pentoxide, in solvent sulphuric acid was a special form of dinitrogen pentoxide, but was not the molecule of the gaseous substance, or of its solutions in non-ionising solvents.

(2.2) *Cryoscopic Proof of the Conversion of Dinitrogen Pentoxide into the Nitronium Ion.*—In view of the conclusion (Section 1.2) that nitric acid is converted in solvent sulphuric acid into fully dissociated nitronium hydrogen sulphate and partly ionised water, the substantial equivalence, by both chemical and Raman-spectroscopic tests, of solutions of nitric acid and of

dinitrogen pentoxide in sulphuric acid, leads to the inference that dinitrogen pentoxide also is converted into nitronium hydrogen sulphate and partly ionised water, though, naturally, with a diminished proportion of water. The approximate equation is as follows:

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + H_3O^+ + 3HSO_4^-$$

This is the equation which would represent the change if the dinitrogen pentoxide were to dissolve in its ionised from, $(NO_2^+)(NO_3^-)$, and then the nitrate ion were to become converted, as it is bound to be by sulphuric acid, into nitric acid, and thence into a second nitronium ion, in accordance with the equation given on p.

The above equation requires a ν-factor of 6 for dinitrogen pentoxide. However, this estimate must be too high because the ions of water, the hydroxonium and hydrogen sulphate ions, will partly recombine (cf. Part II). This effect in principle renders the ν-factor dependent on the concentration. A closer estimate of the ν-factors applying to our concentrations can be obtained by using the determined average ν-factor for water in a similar range of concentrations, and making a rough allowance for the common-ion effects of the simultaneously formed nitronium hydrogen sulphate, just as was done in the case of the solute nitric acid (Section 1.2). This procedure indicates that one should expect ν-factors in the range $5{\cdot}78 \pm 0{\cdot}11$. In our preliminary report on the cryoscopic behaviour of dinitrogen pentoxide in sulphuric acid (*Nature*, **1946**, **158**, 480), we gave the value 5·85, as the experimentally determined ν-factor for this solute. However, this value becomes a little changed as a result of improved constants and better procedures for calculation. The result is to improve the agreement, which definitely establishes the form of ionisation postulated.

(2.3) *Calculation of Theoretical ν-Factors for Dinitrogen Pentoxide.*—This calculation is made by the same method as that illustrated in Section 1.3, though some of the details of the procedure are a little different, because of the altered ratio in which nitronium hydrogen sulphate and water are formed from dinitrogen pentoxide, as compared with the ratio in which they are produced from nitric acid.

It is necessary first to compute ν-factors for total water in molality $m_3 + m_3'$, assuming that water in molality m_3 has first been added in order to repress the self-ionisation of the sulphuric acid, and that dinitrogen pentoxide in molality m_2 has then been introduced, producing extra water in molality m_3' (with $m_3' = m_2$), and nitronium hydrogen sulphate in molality $2m_2$. The formula for the basicity constant of water then becomes

$$K_3 = \{(m_3 + m_3')(\nu_3 - 1)^2 + 2m_2(\nu_3 - 1)\}/(2 - \nu_3)$$

Thus using the value $K_3 = 0{\cdot}72$ g.-mol. kg.$^{-1}$ (cf. Part II), one obtains ν-factors for total water, such as are listed in Table IV. From these, one may proceed to compute the partial depression $\Delta\theta$ of the freezing point due to total water, using the formula

$$\Delta\theta = 5{\cdot}98\nu_3(m_3 + m_3')\{1 - 0{\cdot}0035\bar{\theta} + 2(\overline{m_3 + m_3'})/10{\cdot}20\}$$

By subtracting the partial depressions, calculated for total water in molality $m_3 + m_3'$, from the depression calculated for the water originally added in molality m_3, one obtains the partial depression, called $\Delta\theta'$, corresponding to the water produced from the dinitrogen pentoxide. From these partial depressions, one can now calculate the ν-factors, which we term ν_3', for the water formed from the dinitrogen pentoxide. The equation used is

$$\Delta\theta' = 5{\cdot}98\nu_3'm_3'\{1 - 0{\cdot}0035\bar{\theta}' + 2(m_3 + m_3')/10{\cdot}20\}$$

The whole calculation up to this stage is illustrated by the figures in Table IV. The headings of the Table anticipate what will be pointed out later, *viz.*, that just the same figures hold if the added solute is dinitrogen tetroxide or dinitrogen trioxide.

The final step in the calculation of theoretical ν-factors for dinitrogen pentoxide, tetroxide, or trioxide consists in adding 4·00 to each of the ν′ values given in the last column of Table IV. The addition is made in respect of the two molecules of fully dissociated nitronium or nitrosonium hydrogen sulphate which are assumed to be formed from any of these oxides simultaneously with the one molecule of partly ionised water.

(2.4) *Experimental ν-Factors for Dinitrogen Pentoxide and their Comparison with Theoretical ν-Factors.*—Since our first report (*Nature*, **1946**, **158**, 480), some new cryoscopic measurements in solvent sulphuric acid, leading to a ν-factor for dinitrogen pentoxide, as well as to one for nitric acid, have been reported by Kuhn (*J. Amer. Chem. Soc.*, **1947**, **69**, 1974). For the pentoxide he obtained ν = 5·50, a value which, according to our work, is low, and would be even

lower if recalculated by our methods. For nitric acid he records $\nu = 3{\cdot}97$, a result which is high, and would not be much improved if recalculated.

TABLE IV.

Theoretical ν-factors for water produced from dinitrogen pentoxide, dinitrogen tetroxide, or dinitrogen trioxide, in solvent sulphuric acid containing water.

Molality of added N_2O_{5-x} (m_x).	ν_3 for total water.	Depression by total water ($\Delta\theta$).	Depression by water from N_2O_{5-x} ($\Delta\theta'$).	ν_3' for water from N_2O_{5-x}.	Molality of added N_2O_{5-x} (m_x).	ν_3 for total water.	Depression by total water ($\Delta\theta$).	Depression by water from N_2O_{5-x} ($\Delta\theta'$).	ν_3' for water from N_2O_{5-x}.
Molality of added water (m_x) = 0·050.					Molality of added water (m_x) = 0·070.				
0·00	1·94	0·583°	—	—	0·00	1·92	0·806°	—	—
0·01	1·91	0·688	0·105°	1·74	0·01	1·89	0·909	0·103°	1·70
0·02	1·88	0·790	0·207	1·71	0·02	1·86	1·007	0·201	1·66
0·03	1·85	0·890	0·307	1·69	0·03	1·83	1·104	0·298	1·64
0·04	1·82	0·986	0·403	1·67	0·04	1·81	1·199	0·393	1·62
0·05	1·80	1·083	0·500	1·65	0·05	1·79	1·293	0·487	1·61

Our measurements were made with dinitrogen pentoxide prepared from nitric acid and phosphoric oxide. It was sublimed from excess of phosphoric oxide, and purified by being twice resublimed through phosphoric oxide in ozonised oxygen between room temperature and —80°. A series of cryoscopic results is recorded in Table V.

TABLE V.

Depression of the freezing point of sulphuric acid by added dinitrogen pentoxide. Comparison of experimental and theoretical ν-factors (Expt. 98).

Molality of added water (m_x) = 0·064.

Molality N_2O_5 (Δm_2).	F. p. (° c.).	ν (exptl.).* $n = 0$.	$n = 2$.	$n = 3$.	ν (theor.).	Molality N_2O_5 (Δm_2).	F. p. (° c.).	ν (exptl.). $n = 0$.	$n = 2$.	$n = 3$.	ν (theor.).
—	9·827	—	—	—	—	0·02111	9·086	5·82	5·73	5·69	5·66
0·00614	9·615	5·74	5·67	5·65	5·72	0·02755	8·858	5·83	5·73	5·68	5·64
0·01247	9·395	5·76	5·68	5·65	5·69	0·03452	8·614	5·82	5·70	5·65	5·63

We have calculated the ν-factors both neglecting the effect of solvation of the nitronium salt and also taking this into account, the solvation numbers of 2 and 3 being assumed. In these calculations it is a sufficient approximation to substitute $s_2 = 4$ and $\nu_2 = 6$ in the nearly-unit correction factor of equation (5) of Part I, when solvation is being neglected, and, since $s_2 = 2n + 4$, to write $s_2 = 8$ and $\nu_2 = 6$, and $s_2 = 10$ and $\nu_2 = 6$, where the solvation number n of the nitronium salt is being taken to be 2 and 3, respectively. The sets of ν-factors, calculated from the cryoscopic results with inclusion of the corrections for solvation of the nitronium salt, are to be compared with the theoretical ν-factors given in the last column. These theoretical ν-factors are calculated, as illustrated in Section 2.3, from the already given chemical interpretation of the reactions which take place on dissolving dinitrogen pentoxide in sulphuric acid.

(2.5) *Calculation of a Theoretical Curve for the Freezing-point Depression due to Dinitrogen Pentoxide.*—This calculation is made by the general method already illustrated in Section 1.5 for solute nitric acid. The results of such a calculation for solute dinitrogen pentoxide are given in Table VI, the headings of which anticipate the point, which will be required later, that exactly the same figures apply to the solutes dinitrogen tetroxide and dinitrogen trioxide. The calculation is made for the case in which the sulphuric acid solvent has been pre-treated by the addition of water in 0·07 molal concentration.

Col. 3 of the Table contains the partial depression of freezing point due to the single molecule of water, which is formed from each molecule of dinitrogen pentoxide, and to the pairs of ions into which this water is partly converted in the sulphuric acid solvent. These figures are taken over from Table IV. The next three columns of Table VI contain partial depressions of freezing point calculated as for a quaternary electrolyte, giving the two nitronium and the two hydrogen sulphate ions, which each molecule of dinitrogen pentoxide is assumed to furnish, in addition to the single molecule of water which becomes partly ionised. The depressions given in col. 4 (headed $n = 0$) were calculated by assuming the solvation number n of the nitronium salt to be zero, equation (5) of Part I being employed with the substitutions $s_2 = 2$ and $\nu_2 = 4$, since the formation of one molecule of the quaternary electrolyte needs two molecules of solvent sulphuric

acid. The depressions in cols. 5 and 6 were calculated by assuming the solvation number n of nitronium hydrogen sulphate to be 2 and 3, respectively, the appropriate forms of equation (5) of Part I being employed ($\epsilon_3 = 2n + 2$). The values in the last three columns of Table VI are total depressions, obtained by addition of the relevant partial depressions.

TABLE VI.

Calculated depressions of the freezing-point of sulphuric acid by dinitrogen pentoxide, dinitrogen tetroxide, or dinitrogen trioxide.

Molality of added water (m_3).	Molality of added N_2O_{5-t} (Δm_3).	Freezing-point depressions (°c.). Formed H_2O and its ions.	$2(NO_2)^+(HSO_4)^-$. $n = 0$.	$n = 2$.	$n = 3$.	N_2O_{5-t}. $n = 0$.	$n = 2$.	$n = 3$.
0·070	0·01	0·103	0·240	0·245	0·248	0·343	0·348	0·351
,,	0·02	0·201	0·481	0·494	0·500	0·682	0·695	0·701
,,	0·03	0·298	0·722	0·745	0·756	1·020	1·043	1·054
,,	0·04	0·393	0·963	1·000	1·015	1·356	1·393	1·408
,,	0·05	0·487	1·204	1·257	1·283	1·691	1·744	1·770

The curve for the figures in the penultimate column, corresponding to the solvation number $n = 2$, is shown in Fig. 1 on p. 2513, in association with points representing the observations. It will be seen that there is a close agreement.

(3) *The Solute Dinitrogen Tetroxide.*

(3.1) *Theory of the Condition of Dinitrogen Tetroxide in Sulphuric Acid.*—It was shown, though in a somewhat qualitative manner, by Pinck (*J. Amer. Chem. Soc.*, 1927, **49**, 2536), and has been confirmed in this laboratory, that many aromatic compounds, provided that they are not too easily nitrosated, may be smoothly nitrated by solutions of dinitrogen tetroxide in sulphuric acid, but that, in this process, only one of the two nitrogen atoms of the dinitrogen tetroxide becomes introduced as a nitro-group into the aromatic molecule. Even deactivated aromatic compounds, such as nitrobenzene, may be readily nitrated in this way.

This is a significant result, but no well-supported view about the nature of the solutions of dinitrogen tetroxide in sulphuric acid seems to have been advanced before our preliminary publication (*Nature*, 1946, **158**, 480), in which it was suggested that dinitrogen tetroxide undergoes an ionisation, generally similar to that of dinitrogen pentoxide, but differing from the latter in that the tetroxide gives one nitronium ion and one nitrosonium ion in place of the two nitronium ions given by the pentoxide. We recorded at that time that Dr. D. J. Millen had detected in such solutions of dinitrogen tetroxide both the nitronium ion and the nitrosonium ion, as well as the hydrogen sulphate ion, by the method of Raman spectroscopy; and we submitted cryoscopic evidence that ionisation in the form suggested was substantially complete.

(3.2) *Cryoscopic Proof of the Conversion of Dinitrogen Tetroxide into the Nitronium and Nitrosonium Ions.*—The approximate equation for the postulated ionisation is as follows:

$$N_2O_4 + 3H_2SO_4 = NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$

Apart from the regeneration of a small proportion of water from its ions, this equation would represent the total change if the dinitrogen tetroxide were to dissolve in either of its possible ionic forms $(NO)^+(NO_3)^-$ or $(NO_2)^+(NO_3)^-$; for, in the first case, the nitrate ion would be converted by the sulphuric acid solvent into nitric acid, and thence into the nitronium ion, whilst in the second, the nitrite ion would yield nitrous acid, and thence a nitrosonium ion.

The above equation represents dinitrogen tetroxide as having a ν-factor of 6; but, as was discussed in connexion with the solute dinitrogen pentoxide, we should expect ν-factors of about $5{\cdot}78 \pm 0{\cdot}11$ on account of the balanced reaction between water and the ions which it forms in solvent sulphuric acid. In our preliminary report (*loc. cit.*) we quoted the cryoscopically determined ν-factor of dinitrogen tetroxide as 5·84. The agreement is tolerable; and it is improved in the more refined treatment now to be described. It is diagnostic of the form of ionisation postulated, and shows that the conversion of dinitrogen tetroxide into the nitronium and nitrosonium ions is quantitative in sulphuric acid.

(3.3) *Experimental ν-Factors for Dinitrogen Tetroxide and their Comparison with Theoretical ν-Factors.*—The dinitrogen tetroxide employed in the present experiments was prepared from 70% nitric acid and solid sodium nitrite, the evolved gas being carried in a stream of oxygen through a condenser arranged to retain nitric acid and water, and into a receiver kept at −80°.

Purified by redistillation in oxygen through phosphoric oxide, the tetroxide was collected at −80° as colourless crystals. A concentrated solution of dinitrogen tetroxide in sulphuric acid was made up for convenience in the addition of the tetroxide to the sulphuric acid in the freezing-point cell (cf. Section 1.3 of Part I). The cryoscopic observations, and the relevant calculations, are reported in Table VII.

TABLE VII.

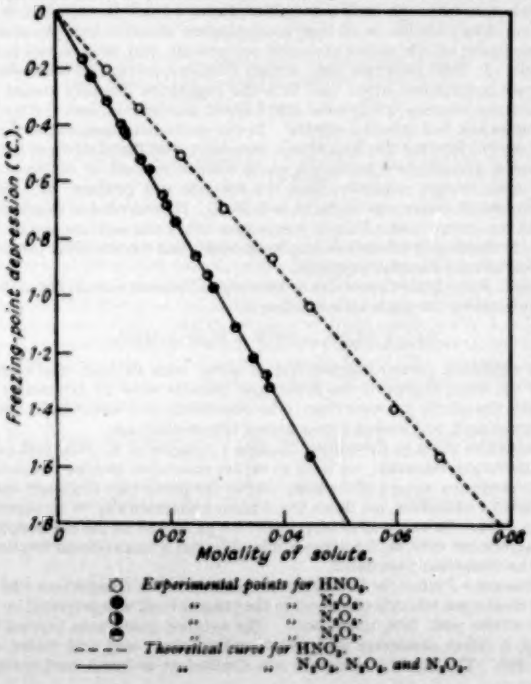
Depression of the freezing point of sulphuric acid by dinitrogen tetroxide. Comparison of experimental and theoretical ν-factors.

Molality of N_2O_4 (Δm_2).	F. p. (° c.).	ν (exptl.). $n = 0$.	$n = 2$.	$n = 3$.	ν (theor.).	Molality of N_2O_4 (Δm_2).	F. p. (° c.).	ν (exptl.). $n = 0$.	$n = 2$.	$n = 3$.	ν (theor.).
Expt. No. 4. Molality of added water (m_1) = 0·075.						Expt. No. 97. Molality of added water (m_1) = 0·069.					
—	9·691	—	—	—	—	—	9·775	—	—	—	—
0·00481	9·524	5·82	5·76	5·73	5·72	0·01144	9·381	5·72	5·64	5·60	5·69
0·01189	9·273	5·82	5·74	5·70	5·69	0·01868	9·130	5·73	5·64	5·59	5·66
0·01637	9·113	5·86	5·76	5·71	5·67	0·02646	8·856	5·76	5·65	5·61	5·64
0·01933	9·012	5·82	5·72	5·68	5·66	0·03677	8·501	5·75	5·61	5·56	5·62
						0·04454	8·217	5·80	5·65	5·57	5·61

The calculations of ν-factors from the experimental results are made exactly as in the case of dinitrogen pentoxide, although, for the purpose of computing the correction for solvation, an estimate had to be made of the solvation number of the nitrosonium ion. We have already

FIG. 1.

Observed depressions of the freezing point of sulphuric acid, and theoretical freezing-point depression curves, for solute nitric acid, and for the solutes dinitrogen pentoxide, tetroxide, and trioxide.



estimated that of the nitronium ion to be close to 2. Taking account not only of the cryoscopic data for dinitrogen tetroxide, but also of those for dinitrogen trioxide which are reported below, we estimate the solvation number of the nitrosonium ion also as approximately 2. The corrected experimental values of ν are given in col. 4 of Table VII. These are to be compared with the theoretical ν-factors entered in the last column of the Table. As is noted in Section 3.2, the theoretical ν-factors for dinitrogen tetroxide, *i.e.*, those required by the postulated form of ionisation of this substance, may be calculated in the same way as for dinitrogen pentoxide.

Another form of comparison between theory and experiment is illustrated in Fig. 1 (p. 2513). As was noted in Section 2.5, a theoretical curve for the depression of freezing point produced by dinitrogen tetroxide may be calculated exactly as for dinitrogen pentoxide; it is, in fact, the same curve. This curve appears in the figure, as also do the points which represent the observed depressions given in Table VII. The agreement is evidently satisfactory.

(4) *The Solute Dinitrogen Trioxide.*

(4.1) *Theory of the Condition of Dinitrogen Trioxide in Sulphuric Acid.*—It was first suggested by Hantzsch and Berger (*Z. anorg. Chem.*, 1930, **190**, 321) that the substance long known as nitrosylsulphuric acid, or "chamber crystals," has the ionic constitution of nitrosonium hydrogen sulphate, $(NO^+)(HSO_4)^-$. Their evidence for this structure was derived from the cryoscopically determined molecular weight in sulphuric acid solution, from comparisons with other nitrosonium salts, such as the perchlorate, and from the fact that solutions of the substance in sulphuric acid nitrosate, but do not nitrate, suitable aromatic compounds, such as dimethylaniline. The fundamental Raman frequency of the nitrosonium ion was found by Angus and Leckie in solid nitrosonium hydrogen sulphate, and also in nitrosonium perchlorate; and they found it again in solutions of chamber crystals in sulphuric acid (*Proc. Roy. Soc.*, 1935, *A*, **149**, 327; *A*, **150**, 615).

Dinitrogen trioxide, although itself a deep blue, forms a colourless solution in sulphuric acid. Such solutions are closely similar in all their more obvious chemical and physical properties, for instance, in their power of nitrosating aromatic compounds, and, as is shown in detail in an accompanying paper (*J.*, 1950, paper no. 508), in their Raman spectrum, to solutions of nitrosonium hydrogen sulphate in sulphuric acid; and thus the suggestion becomes almost inevitable that solutions of dinitrogen trioxide in sulphuric acid contain nitrosonium ions and hydrogen sulphate ions as the characteristic and essential solutes. In our preliminary account of this work (*Nature*, 1946, **158**, 480), we put forward this hypothesis, supposing that the dinitrogen trioxide undergoes in sulphuric acid a quantitative ionisation quite similar to that of dinitrogen pentoxide or dinitrogen tetroxide, except, naturally, that the trioxide will produce two nitrosonium ions instead of two nitronium ions or one cation of each kind. We recorded at that time that Dr. D. J. Millen had found the characteristic Raman frequencies of the nitrosonium and hydrogen sulphate ions in solutions of dinitrogen trioxide in sulphuric acid; and we ourselves presented cryoscopic evidence in favour of the ionisation suggested.

(4.2) *Cryoscopic Proof of the Conversion of Dinitrogen Trioxide into the Nitrosonium Ion.*—The approximate equation for the assumed ionisation is

$$N_2O_3 + 3H_2SO_4 = 2NO^+ + H_3O^+ + 3HSO_4^-$$

Apart from the neglected partial regeneration of water from its ions, this equation expresses what would be the total change if the dinitrogen trioxide were to dissolve in its ionic form $(NO^+)(NO_2^-)$, and the nitrite ion were then to be converted, as it would be in the sulphuric acid solvent, into nitrous acid, and thence into a second nitrosonium ion.

The above equation gives to dinitrogen trioxide a ν-factor of 6; but, just as for dinitrogen pentoxide and dinitrogen tetroxide, we have to expect somewhat smaller ν-factors, owing to the balanced reaction between water and its ions. As in the previously discussed cases, we may, in advance of detailed calculation, set down the ν-factors theoretically to be expected as lying in the range $5{\cdot}78 \pm 0{\cdot}11$. In our preliminary report we gave 5·85 as the cryoscopically estimated ν-factor. The agreement even at this stage is tolerable, but a more refined treatment establishes with precision the ionisation postulated.

(4.3) *Experimental ν-Factors for Dinitrogen Trioxide and their Comparison with the Theoretical ν-Factors.*—The dinitrogen trioxide employed in the present work was prepared by the interaction of solid sodium nitrite with 70% nitric acid. The evolved gases were carried in a stream of nitrogen through a reflux condenser arranged to retain nitric acid and water, and were then condensed at −80°. The liquid condensate was distilled at as low a temperature as possible,

in a fairly rapid stream of dry nitric oxide, through phosphoric oxide; and it was again condensed at −80°. Dry nitric oxide was passed for some hours through the condensate, which was preserved at −80° in an atmosphere of nitric oxide.

Owing to the tendency of dinitrogen trioxide to decompose when allowed to become warm, some difficulty was experienced in the preparation of those concentrated solutions of known composition of dinitrogen trioxide in sulphuric acid which were required as a means for the addition of accurately weighed amounts of dinitrogen trioxide to the sulphuric acid in the freezing-point cell (cf. Section 1.3, Part I). Our attempts to prepare such solutions by direct addition, *i.e.*, by the addition of liquid dinitrogen trioxide at −80° to solid sulphuric acid, the whole being then allowed to warm to above the eutectic temperature in a closed tube until the liquid contents of the tube became homogeneous, always produced small residues of unabsorbed nitric oxide. This meant that a little of the dissolved material was dinitrogen tetroxide, and that therefore a measurement of the increase in weight of the solution above that of the originally used solvent would not give accurately the molecular composition of the solution. Dr. Millen was usually able to find in the Raman spectra of solutions prepared by this method a faint but distinct record of the characteristic frequency of the nitronium ion, besides, of course, a strong record of the fundamental frequency of the nitrosonium ion. The effect of the disturbance was also easily detectable in our cryoscopic measurements with these solutions, which gave non-reproducible ν-factors always from 1% to 5% too low.

Correct results were obtained when the dinitrogen trioxide was carried into the sulphuric acid by distillation in a stream of dry nitric oxide at the lowest convenient temperatures. The solution in the sulphuric acid absorbs a little of the nitric oxide with the formation of a pale violet colour; but this nitric oxide is at once evolved with discharge of the colour when, after the transference, the nitric oxide atmosphere above the sulphuric acid is replaced, first by nitrogen, and then by dry air, in preparation for the final weighing. Some cryoscopic results obtained by this method are recorded in Table VIII.

TABLE VIII.

Depression of the freezing point of sulphuric acid by dinitrogen trioxide. Comparison of experimental and theoretical ν-factors (Expt. 101).

Molality of added water (m_a) = 0·070.

Molality of N_2O_3 (Δm_s).	F. p. (° c.).	ν (exptl.). $n = 0$.	$n = 2$.	$n = 3$.	ν (theor.).	Molality of N_2O_3 (Δm_s).	F. p. (° c.).	ν (exptl.) $n = 0$.	$n = 2$.	$n = 3$.	ν (theor.).
—	9·758	—	—	—	—	0·02448	8·904	5·79	5·68	5·63	5·65
0·00901	9·446	5·75	5·68	5·64	5·70	0·03140	8·651	5·86	5·73	5·68	5·63
0·01498	9·237	5·77	5·68	5·64	5·68	0·03754	8·441	5·83	5·69	5·63	5·62

The calculations of the ν-factor are made exactly as for dinitrogen pentoxide and dinitrogen tetroxide. The ν-factors calculated with the solvation number $n = 2$ for nitrosonium hydrogen sulphate are in columns 4 and 8 of the Table; and they are to be compared with the theoretical ν-factors. These are calculated from the postulated chemical changes, as described in Section 2.3.

The comparison between theory and experiment is shown again in Fig. 1. As was noted in Section 2.5, the theoretical curves for the depression of the freezing point of sulphuric acid by dinitrogen pentoxide, tetroxide, and trioxide are identical. The diagram shows that the observational points for dinitrogen trioxide, no less than those for the tetroxide and the pentoxide, lie well on this common curve.

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500. *Cryoscopic Measurements in Sulphuric Acid. Part IV. Reactions of Ionised Sulphates in Sulphuric Oleum. Self-ionisation Equilibria in Sulphuric Acid, and Ionic Equilibria in Oleum. The Polysulphuric Acids.*

By R. J. Gillespie.

The variations of freezing point have been followed when, to an oleum, first ammonium sulphate, and thereafter water, are added. The nature of the results can be appreciated by reference to Fig. 1 on p. 2521. The freezing points of originally taken oleums lie on the limiting curve towards the right. The freezing-point curves obtained by adding ammonium sulphate run generally downward towards the left, but with a reduced initial slope, the initial reduction increasing, and leading eventually to an initial rise in the curve, as the concentration of the original oleum is increased. The curves for the addition of water are those which start upwards towards the left, then pass through a maximum, and then descend.

From these results the basicity constant of the hydrogen disulphate ion is deduced. From this, and the acidity constant of disulphuric acid, the autoprotolysis constant of sulphuric acid is calculated. By combining this value with the total concentration of self-dissociation products in sulphuric acid, as derived in Part II, the concentrations are computed of each of the four ionic species formed by self-dissociation of sulphuric acid. The dissociation consists of an autoprotolysis to $H_3SO_4^+$ and HSO_4^-, accompanied by a smaller amount of ionic self-dehydration to H_3O^+ and $HS_2O_7^-$.

Another set of conclusions relates to the presence in oleum, besides disulphuric acid, $H_2S_2O_7$, of higher polysulphuric acids. Trisulphuric acid, $H_2S_3O_{10}$, and tetrasulphuric acid, $H_2S_4O_{13}$, are definitely recognised. An equilibrium constant governing the formation of trisulphuric acid is deduced. The property of forming poly-acids, for which tungsten and molybdenum are notable, is thus extended to sulphur, to which it can be traced through the intermediate elements, chromium and selenium, as well as, in the other direction, to uranium. Therefore it appears as a somewhat general property of the elements in Group VI.

Further conclusions are drawn concerning the strengths of the polysulphuric acids. Disulphuric acid was shown in Part II to be a semi-strong acid. The hydrogen disulphate ion is, however, a very weak acid. It is very incompletely deprotonated to form a doubly charged ion, even by a large excess of hydrogen sulphate ion, the strongest available base in these solutions. Thus disulphuric acid does not undergo, to any marked extent, a second stage of ionisation, before the first stage is practically complete. On the other hand, the higher polysulphuric acids appear to be somewhat stronger than disulphuric acid with respect to first stages of ionisation, and to be very much stronger with respect to second stages. This is reasonable on structural and electrostatic grounds. Thus, on the progressive addition of hydrogen sulphate ions, the higher polysulphuric acids are deprotonated earlier than is the disulphuric acid; and the doubly charged anions of the higher poly-acids are formed in much greater proportion than is the doubly charged anion of disulphuric acid.

The reactions taking place during the titration of sulphur trioxide in oleum, or in solutions in oleum, with water to the cessation of fuming (Brand), are considered. The suggestion that one hydrogen sulphate ion removes half a molecule of titratable sulphur trioxide, for the reason that two hydrogen sulphate ions suffice for a stoicheiometrically quantitative removal of two protons from one molecule of disulphuric acid, is shown to be unfounded. The factor one-half is an approximation, and depends on an arbitrary adjustment (mainly through temperature control) of the sensitivity of the end-point of the titration, *i.e.*, it depends on an adjusted relation between the minimum concentration of disulphuric acid required to produce a visible fuming, and the basicity constant (which has the dimensions of concentration) of the hydrogen disulphate ion.

(I) *Preliminary Statements about the Species Present in Sulphuric Acid and in Dilute Oleum.*

(1.1) *The Self-dissociation of Sulphuric Acid.*—The work to be reported was undertaken in order to obtain further information about the molecular and ionic species which are present, and about the equilibria in which they participate, in solvent sulphuric acid and in dilute sulphuric oleum. In order to simplify the following account of the relationships which the measurements reveal, it is convenient to commence with some statements which partly summarise results described in preceding papers, but partly also anticipate, or indicate, findings established later in this paper.

The rounding of the freezing-point curve of the system H_2O–SO_3 at compositions in the neighbourhood of H_2SO_4 was discussed in Part II (*J.*, 1950, 2493). It shows that sulphuric acid is considerably self-dissociated. Undoubtedly the self-dissociation is partly an autoprotolysis. The products of this process are the sulphuric acidium ion and the hydrogen sulphate ion :

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The process is thus quite analogous to the autoprotolyses that occur in other solvents, such as water and ammonia.

A part of the process of self-dissociation of sulphuric acid must, however, arise from the self-dehydration of the sulphuric acid to sulphur trioxide and water, each of which reacts with sulphuric acid to produce ions, as already described in Part II :

$$\left.\begin{aligned} H_2SO_4 &= H_2O + SO_3 \\ H_2SO_4 + SO_3 &= H_2S_2O_7 \\ H_2SO_4 + H_2S_2O_7 &= H_2SO_4^+ + HS_2O_7^- \\ H_2SO_4 + H_2O &= H_3O^+ + HSO_4^- \end{aligned}\right\} \quad \ldots\ldots\ldots (2)$$

Qualitatively, the formation of sulphur trioxide is indicated by the fuming of pure sulphuric acid just above room temperature (cf. Brand, *J.*, 1946, 585). The formation of disulphuric acid from sulphur trioxide and sulphuric acid is well established, and so also are the ionisations of disulphuric acid and of water.

It will be shown later that sulphur trioxide and sulphuric acid can combine in molecular ratios other than 1 : 1, and that they are thus able to produce a whole series of ionising polysulphuric acids. However, these more complex ionogenic reactions of sulphur trioxide are not important at the low concentrations which are relevant to the self-dissociation of pure sulphuric acid. Furthermore, in the approximation to which one is limited by other considerations, it may be taken that, in accordance with equations (2), disulphuric acid is completely ionised as an acid, and water is completely ionised as a base, at the concentrations in which these substances are formed by self-dissociation. It follows that equations (2) can be reduced to the following approximate form :

$$2H_2SO_4 = H_3O^+ + HS_2O_7^- \quad \ldots\ldots\ldots\ldots (3)$$

In this approximation, the total self-dissociation of sulphuric acid can therefore be described by means of two equilibrium constants corresponding to equations (1) and (3). They are the autoprotolysis constant,

$$K_{ap} = [H_2SO_4^+][HSO_4^-]$$

and the ionic self-dehydration constant,

$$K_{id} = [H_3O^+][HS_2O_7^-]$$

It was established in Part II that, in pure sulphuric acid at its freezing point, the total concentration of all the products of dissociation is 0·43 molal, *i.e.*, enough to lower the freezing point by 0·26°. In Part I it was shown that the products of the autoprotolysis alone lower the freezing point by 0·16°; and hence it can be concluded that the concentration of the products of the self-dehydration is sufficient to cause a freezing-point lowering of 0·10°. The total self-dissociation is thus analysed into the following parts, and the manner in which they contribute to the lowering of the freezing point from 10·62°, as estimated for non-dissociated sulphuric acid, to the actual freezing point, 10·36°, of the self-dissociated acid in equilibrium, is as shown :

$[H_2SO_4^+] = [HSO_4^-] = 0{\cdot}013$ molal. Total 0·026 molal. Depression 0·16°.
$[H_3O^+] = [HS_2O_7^-] = 0{\cdot}0083$ molal. Total 0·017 molal. Depression 0·10°.
All products of self-dissociation . . . 0·043 molal. Depression 0·26°.

From these data, we can calculate the following values for the autoprotolysis constant and the ionic self-dissociation constant, at the freezing point of pure sulphuric acid, 10·36° :

$$K_{ap} = 0{\cdot}00017 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$
$$K_{id} = 0{\cdot}00007 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

The present experiments were designed independently to confirm these conclusions concerning the self-dissociation. Although the phenomena which provide the basis for the analysis to be described are observed in combination with effects arising from the formation and ionisation of higher polysulphuric acids, the desired confirmation has been secured. (We shall find it convenient, for the purpose of illustrating computing procedures, to utilise the above estimates of the autoprotolysis and ionic self-dehydration constants, even though we shall later derive the same values for these two quantities in an independent way.)

(1.2) *The Species present in Dilute Oleum.*—The known phase-diagram for the system H_2O–SO_3 indicates the existence of only one solid phase having a composition intermediate between that of sulphuric acid and that of sulphur trioxide, *viz.*, disulphuric acid, $H_2S_2O_7$. On

this account it has usually been assumed that sulphur trioxide in solution in sulphuric acid is largely converted into disulphuric acid.

As to dilute solutions of sulphur trioxide in sulphuric acid, this is undoubtedly true. In Part II it was found that a provisional first ionisation constant of disulphuric acid could be calculated if it were assumed that, at concentrations of the order of 0·1 molal, sulphur trioxide is converted almost entirely into disulphuric acid, and that, at such concentrations, only the first ionisation constant of this acid is of importance.

However, it will here be shown that this description provides only an approximate account of the behaviour of such solutions. Certainly, solutions in sulphuric acid of sulphur trioxide in concentrations of the order of 0·1 molal or somewhat stronger contain mainly disulphuric acid in its molecular and ionic forms; but such solutions also contain appreciable proportions of higher polysulphuric acids, notably trisulphuric acid, $H_2S_3O_{10}$, and tetrasulphuric acid, $H_2S_4O_{13}$. These acids belong to the series $H_2O(SO_3)_n$, concerning which little information has hitherto been available, except in relation to the first two members, sulphuric and disulphuric acids.

With regard to its first ionisation, disulphuric acid is an acid of moderate strength in solvent sulphuric acid (cf. Part II). Still with reference to first ionisations, we must, on general electrostatic grounds, expect the higher polysulphuric acids to be rather stronger acids than disulphuric acid. In Part II it was shown that disulphuric acid, at concentrations of the order of 0·1 molal in sulphuric acid, is considerably ionised with respect to its first stage of ionisation. It is established in this paper that the higher polysulphuric acids, which are present in such solutions, are ionised quite largely with respect to their first stages of ionisation, and are even further ionised as noted below.

On general electrostatic grounds, we must expect that, as the chain $\cdot[SO_2\cdot O]_n\cdot$ lengthens in a higher polysulphuric acid, *i.e.*, as n increases, the second ionisation constant of the acid will rapidly become more nearly comparable to the first. The second ionisation constant of disulphuric acid is undoubtedly much smaller than the first; for we have no evidence that any appreciable proportion of the normal disulphate ion can coexist with molecular disulphuric acid. On the other hand, it will be shown that at least some of the polysulphuric acids which are present in dilute oleum, notably trisulphuric acid and tetrasulphuric acid, are considerably ionised with respect to both their stages of acidic ionisation.

(2) *Freezing Point of Solutions of Ammonium Sulphate in Dilute Oleum. Solvolysis of the Hydrogen Disulphate Ion. Formation and Ionisation of Polysulphuric Acids.*

(2.1) *The i-Factors of Ammonium Hydrogen Disulphate.*—In the experiments now to be described, the freezing point was measured as successive portions of ammonium sulphate were added to dilute oleums of various initial strengths. Ammonium sulphate is completely ionised (cf. Part I, *J.*, 1950, 2473) in sulphuric acid, according to the following equation :

$$(NH_4)_2SO_4 + H_2SO_4 = 2NH_4^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As an initial simplification, we assume that the sulphur trioxide, which with sulphuric acid composes the oleum, is present entirely as disulphuric acid, which is ionising as an acid according to the following balanced reaction :

$$H_2S_2O_7 + H_2SO_4 = HS_2O_7^- + H_3SO_4^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Then the first effect of the added salt must be to destroy the sulphuric acidium ion $H_3SO_4^+$ by combination with hydrogen sulphate ion (cf. equation 1), and thus to replace the former ion by its equivalent of ammonium ion. When 0·5 mol. of ammonium sulphate has been added for every original mol. of disulphuric acid, then stoicheiometrically sufficient hydrogen sulphate ions will have been produced to secure the conversion of the whole of the disulphuric acid into ammonium hydrogen disulphate. The reaction may be formulated as a simple acid-to-base proton-transfer :

$$H_2S_2O_7 + HSO_4^- = HS_2O_7^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The solution now has the analytical composition of a solution of ammonium hydrogen disulphate in sulphuric acid, whether reaction (6) goes to completion or not. If reaction (6) were to proceed to completion, then the solution would contain two ions, the ammonium ion and the hydrogen disulphate ion, for every stoicheiometric molecule of ammonium hydrogen disulphate, *i.e.*, it would contain two ions for every original stoicheiometric molecule of disulphuric acid, or of sulphur trioxide.

Our interest at present is in the lack of completeness of reaction (6). Any such lack of completeness constitutes a partial solvolysis of the hydrogen disulphate ion—its acceptance of a proton from the solvent. The effect of the solvolysis on the total solutes is to replace a hydrogen disulphate ion by a disulphuric acid molecule and a hydrogen sulphate ion, *i.e.*, to replace one solute particle by two. Hence the effect is to create in the solution a total of more than two solute particles for every original stoicheiometric molecule of disulphuric acid. A quantitative solvolysis would produce a total of three solute particles for each molecule of disulphuric acid.

TABLE I.

Freezing point of solutions of ammonium sulphate in dilute oleum.

	Weight (g.).				Molality.		F. p.
Solution.	Am_2SO_4.	H_2SO_4.	$H_2S_2O_7$.	$AmHS_2O_7$.	$H_2S_2O_7$.	$AmHS_2O_7$.	(° c.).
Expt. 10 * :							
—	—	109·13	4·273	—	0·2200	—	8·860
0·410	0·0789	109·50	4·077	0·2334	0·2092	0·0108	8·858
0·558	0·1864	110·02	3·805	0·5506	0·1943	0·0257	8·849
0·815	0·3432	110·47	3·397	1·104	0·1728	0·0452	8·805
0·715	0·4879	111·08	3·028	1·435	0·1531	0·0669	8·755
1·030	0·6861	112·40	2·546	2·027	0·1273	0·0927	8·677
0·994	0·8758	113·41	2·072	2·587	0·1027	0·1173	8·572
1·079	1·083	114·30	1·547	3·200	0·0755	0·1445	8·451
0·958	1·267	115·18	1·083	3·743	0·0526	0·1674	8·307
1·065	1·473	116·37	0·576	4·352	0·0277	0·1923	8·159
1·065	1·678	117·13	0·047	4·958	0·0032	0·2178	7·983
				$AmHSO_4$.		$AmHSO_4$.	
1·050	1·880	117·95	0·000	0·322	0·0000	0·0283	7·795
1·637	2·190	119·04	0·000	0·862	0·0000	0·0630	7·478
1·654	2·504	120·14	0·000	1·409	0·0000	0·1020	7·153
Expt. 11 † :							
				$AmHS_2O_7$.		$AmHS_2O_7$.	
—	—	103·81	7·354	—	0·3980	—	7·660
0·750	0·1443	104·49	6·908	0·4265	0·3713	0·0267	7·678
1·626	0·4572	105·84	6·250	1·351	0·3318	0·0662	7·679
2·978	1·030	108·60	4·862	3·044	0·2514	0·1466	7·539
2·306	1·474	110·68	3·790	4·355	0·1924	0·2056	7·351
4·269	2·295	114·50	1·798	6·783	0·0809	0·3090	6·844
3·464	2·962	117·60	0·188	8·751	0·0090	0·3890	6·541
H_2O added.			H_2O.		H_2O.		
0·682	,,	118·15	0·063	—	0·0295	—	6·429
0·088	,,	118·63	0·151	—	0·0767	—	6·498
0·243	,,	119·95	0·394	—	0·1824	—	6·520
0·298	,,	121·58	0·692	—	0·3162	—	6·311
0·166	,,	122·48	0·858	—	0·3893	—	5·891
Expt. 12 ‡ :							
Soln. added.			$H_2S_2O_7$.		$H_2S_2O_7$.		
—	—	104·56	4·281	—	0·2300	—	8·800
2·867	0·6249	107·00	2·682	1·866	0·1408	0·0892	8·618
3·874	1·469	110·43	0·527	4·341	0·0281	0·2019	8·027
H_2O added.			H_2O.		H_2O.		
0·056	,,	111·01	0·0027	—	0·0014	—	8·125
0·056	,,	111·53	0·0587	—	0·0293	—	8·200
0·106	,,	111·91	0·165	—	0·0819	—	8·283
0·080	,,	112·34	0·245	—	0·1212	—	8·303
0·108	,,	112·93	0·353	—	0·1737	—	8·248
0·111	,,	112·93	0·464	—	0·2283	—	7·877
0·112	,,	112·93	0·576	—	0·2834	—	7·273

* Ammonium sulphate was added as a solution in the original oleum solvent. The weights in the first column are those of the added solution. The composition of the solution used for the first 11 additions was as follows: 22·735 g. of oleum; 5·420 g. of Am_2SO_4. The last 2 additions were made with a solution of the following composition: 30·887 g. of oleum; 7·231 g. of Am_2SO_4.

† The weights in col. 1 (first six entries) are those of an added solution of ammonium sulphate in the original oleum. The composition of this solution was as follows: 25·575 g. of oleum; 6·995 g. of Am_2SO_4.

‡ The added solution (col. 1) had the following composition: 25·235 g. of original oleum; 7·032 g. of Am_2SO_4.

TABLE I.—*continued.*

Weight (g.).					Molality.		
Am_2SO_4 added.	Am_2SO_4 total.	H_2SO_4.	$H_2S_2O_7$.	$AmHS_2O_7$.	$H_2S_2O_7$.	$AmHS_2O_7$.	F. p. (° c.).
Expt. 104 :							
—	—	123·63	3·6734	—	0·1670	—	9·238
0·1394	0·1394	123·73	3·298	0·4120	0·1498	0·0272	9·203
0·1569	0·2963	123·85	2·875	0·8755	0·1304	0·0766	9·157
0·4341	0·7304	124·17	1·705	2·158	0·0771	0·0899	8·963
0·5144	1·2448	124·55	0·317	3·677	0·0143	0·1527	8·596
				$AmHSO_4$.		$AmHSO_4$.	
0·1696	1·3144	124·59	0·000	0·0906	0·0000	0·0063	8·443
0·1966	1·5210	124·45	,,	0·4322	,,	0·0303	8·242
0·2742	1·7952	124·24	,,	0·7110	,,	0·0638	7·949
Expt. 105 :				$AmHS_2O_7$.		$AmHS_2O_7$.	
—	—	117·84	3·316	—	0·1580	—	9·328
0·2695	0·2695	118·04	2·589	0·6962	0·1232	0·0348	9·258
0·7545	1·0240	118·60	0·555	3·024	0·0263	0·1317	8·787
				$AmHSO_4$.		$AmHSO_4$.	
0·3884	1·4124	118·61	0·000	0·3181	0·0000	0·0233	8·407
0·3290	1·7414	118·37	,,	0·8912	,,	0·0655	8·030
0·2719	2·0133	118·17	,,	1·365	,,	0·1004	7·697
Expt. 106 :				$AmHS_2O_7$.		$AmHS_2O_7$.	
—	—	126·84	3·230	—	0·1430	—	9·409
0·5971	0·0571	127·28	1·620	1·764	0·0715	0·0715	9·183
0·2315	0·8286	127·45	0·996	2·448	0·0439	0·0991	9·039
0·1291	0·9577	127·55	0·648	2·830	0·0285	0·1145	8·950
H_2O added.							
0·0358	0·9577	127·94	0·294	—	0·0129	—	9·015
			H_2O.		H_2O.		
0·0683	,,	128·47	0·0386	—	0·0166	—	9·115
0·0654	,,	128·83	0·1040	—	0·0448	—	9·189
0·0659	,,	129·19	0·1699	—	0·0731	—	9·230
0·0830	,,	129·64	0·2529	—	0·1083	—	9·194
0·0824	,,	130·08	0·3353	—	0·1432	—	8·933
0·1169	,,	130·72	0·4522	—	0·1922	—	8·386

Before considering the experimental evidence on this matter, let us note that there is an alternative cause which could lead to the appearance of more than two solute particles for each original molecule of disulphuric acid. Such a result could arise, not only if the hydrogen disulphate ion received a proton from the solvent, but also if it donated a proton to the solvent :

$$HS_2O_7^- + H_2SO_4 = S_2O_7^{--} + H_3SO_4^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

However, it will be shown in Sections 2.3 and 3.1 that such an interpretation cannot be entertained. For a body of evidence exists to the effect that the hydrogen disulphate ion can transfer its proton only to a quite limited extent even to the hydrogen sulphate ion, which is the strongest base that can be supplied in any considerable concentration in solvent sulphuric acid. Therefore it is inconceivable that the hydrogen disulphate ion should transfer its proton to the sulphuric acid molecule to such an extent that the normal disulphate ion and the sulphuric acidium ion would have to co-exist each in appreciable concentration.

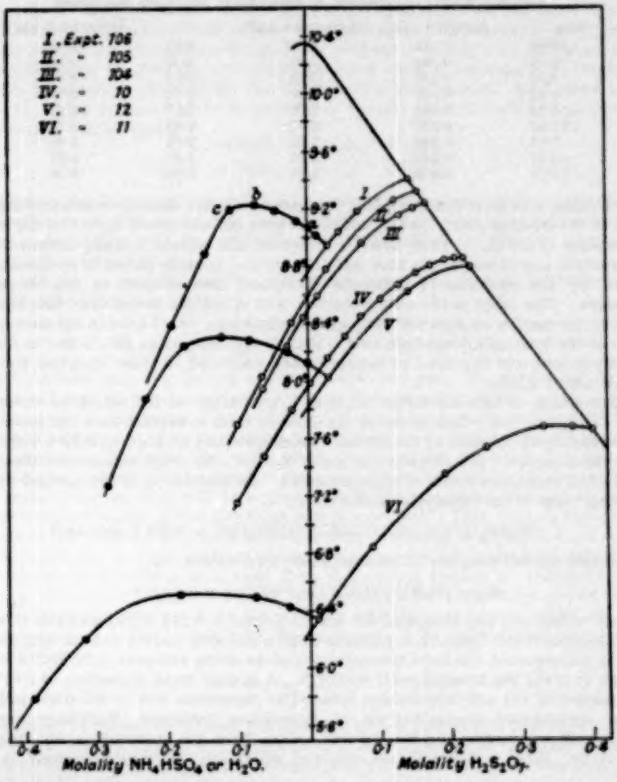
Table I contains the record of such cryoscopic observations as are required for the discussion given in Sections 2 and 3 of this paper.

These results are represented in Fig. 1. On the right-hand side (" acidic " side) of the central line, freezing points are plotted against the molality of disulphuric acid, calculated on the assumption that all the sulphur trioxide, which with sulphuric acid composes the oleum, is present in this form. The vertical line (" neutral " line) corresponds to the composition of the solvent sulphuric acid, or of solutions, in that solvent, whose compositions can be expressed entirely in terms of " neutral " salts, such as ammonium hydrogen disulphate. On the left-hand side (" basic " side) of the neutral line, the freezing points are plotted against the molality of hydrogen sulphate ion, calculated on the assumption that it is produced in a completed reaction between the solvent and either added ammonium sulphate or added water; and that it is destroyed in a completed reaction with any disulphuric acid originally present (cf. equation 6).

The freezing points of the original oleums, to which successive amounts of ammonium sulphate were added in the different experiments, are shown upon the nearly straight curve which slopes downward towards the right in Fig. 1 (cf. Fig. 1 of Part II, where the same curve is on the left of the diagram). The effect of the added ammonium sulphate on the freezing point is shown by the curves which, starting out from the nearly straight curve, slope generally downward towards the left, though with an initial bend-over, the significance of which will be considered in Section 2.2.

FIG. 1.

Freezing points of solutions of ammonium sulphate in dilute oleums.



● *Freezing points after the addition of* H_2O. ○ *Freezing points after the addition of* $(NH_4)_2SO_4$.

In some experiments, ammonium sulphate was added in quantity more than sufficient to react with all the original stoicheiometric disulphuric acid. In other experiments the ammonium sulphate was added in rather less than the amount necessary for this reaction, and then the excess of disulphuric acid was removed by adding water, and the addition of water was continued further. The water curves are those which, starting from points just to the right of the neutral line, slope upwards to the left, then pass through a maximum, and then descend; curves like these have previously been obtained by Poma (*J. Chim. physique*, 1912, **10**, 177).

We shall consider first the points at which the various curves cut the neutral line. At these

points the solutions all have the analytical compositions of solutions of ammonium hydrogen disulphate. At the points at which the ammonium sulphate curves, produced if necessary, cut the neutral line, the molality of the ammonium hydrogen disulphate is equal to that of the stoicheiometric disulphuric acid in the initially employed oleum. At the points at which water curves cut the neutral line, the molality of the ammonium hydrogen disulphate is equal to that of such of the original disulphuric acid as was destroyed by the added ammonium sulphate. The molalities and freezing points of all these solutions of ammonium hydrogen disulphates are assembled in Table II.

TABLE II.

Freezing points of solutions of ammonium hydrogen disulphate.

Expt. no.	F. p. (° c.).	Molality (Δm).	Depression ($\Delta\theta'$).	ν'.	Depression ($\Delta\theta''$).	ν''.
106	9·06	0·115	1·56°	2·27	1·48°	2·14
	8·74	0·143	1·88	2·19	1·81	2·10
105	8·59	0·158	2·03	2·15	1·97	2·08
104	8·45	0·167	2·14	2·14	2·08	2·07
12	8·12	0·202	2·60	2·07	2·45	2·02
	7·83	0·230	2·79	2·03	2·74	1·99
10	7·97	0·240	2·85	2·02	2·80	1·98
11	6·37	0·389	4·25	1·84	4·21	1·82
	6·28	0·398	4·34	1·84	4·30	1·82

In this Table, a series of freezing-point depressions $\Delta\theta'$, are entered, which are computed with reference to the freezing point, 10·62°, which the pure solvent would have if it did not undergo self-dissociation (Part II, *J.*, 1950, 2493). However, the solvent actually suffers two forms of self-dissociation, one of which, the ionic self-dehydration, is easily shown to be almost competely suppressed by the amounts of hydrogen disulphate ions present in the solutions under consideration. The other is the autoprotolysis, and it will be shown that this is only partly repressed by the smaller amounts of hydrogen sulphate ions, which arise in the same solutions by solvolysis of the hydrogen disulphate ions. Part of the depression, $\Delta\theta'$, is due to the surviving autoprotolytic ions, and this must be calculated and deducted, in order to obtain the depression due to the added solute.

The calculation of this correction requires a knowledge of the solvolysis constant of the hydrogen disulphate ion, which is one of the data we wish to extract from the results, and also of the autoprotolysis constant of the solvent, which quantity we hope to derive with the help of the solvolysis constant. It is therefore necessary to start with rough estimates of these quantities and proceed by successive cycles of approximation. In illustration of the method we may take the following value of the solvolysis constant, *viz.*,

$$K_s(HS_2O_7^-) = [H_2S_2O_7][HSO_4^-]/[HS_2O_7^-] = 0{\cdot}008 \text{ g.-mol. kg.}^{-1}$$

and the already quoted estimate of the autoprotolysis constant, *viz.*,

$$K_{ap} = [H_2SO_4^+][HSO_4^-] = 0{\cdot}00017 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

From these values one can compute, for instance, that a 0·115 molal solution of ammonium hydrogen disulphate (cf. Table II, top line) is 0·030 molal with respect to hydrogen sulphate ion, and that, in consequence, the total concentration of surviving autoprotolytic ions is 0·012 molal, *i.e.*, enough to lower the freezing point by 0·07°. A further small correction of 0·01° has to be made in respect of the self-dehydration ions. The depression due to self-dissociation ions at the other investigated concentrations of ammonium hydrogen disulphate are similarly calculated, and, by subtracting the derived values from the depressions $\Delta\theta'$, the corrected depressions $\Delta\theta''$, listed in Table II, are obtained, which are attributable entirely to the added solute.

From the depressions $\Delta\theta'$ and $\Delta\theta''$, the van't Hoff factors for ammonium hydrogen disulphate, ν' and ν'' respectively, have been calculated, using equation (4) of Part I (*J.*, 1950, 2473), with the values, $\nu_2 = 2$, $s_2 = 1$, and $m_2 = 0$, substituted in the nearly-unit correction factor. The substitution $s_1 = 1$ assumes the solvation number of ammonium hydrogen disulphate to be the same as that of ammonium hydrogen sulphate, namely, one (Part I, *loc. cit.*).

Both sets of van't Hoff factor are given in Table II, because the ν'' values are, in principle at least, and probably in practice, over-corrected, though it is difficult to estimate the error. The reason for the error is that the solutions must contain, besides such hydrogen sulphate ion as is derived from the solvolysis of the hydrogen disulphate ion, some additional hydrogen sulphate ion arising from the formation and partial solvolysis of the anions of the higher polysulphuric

acids, a matter which is next to be considered. This extra hydrogen sulphate ion will reduce the concentration of surviving autoprotolytic ions, thus rendering our correction too large.

At the lowest concentrations of ammonium hydrogen disulphate the ν-factors rise above 2, thus indicating a certain amount of solvolysis of the anion. At the higher concentrations, however, the ν-factors fall below 2, and we have to consider the significance of this effect. It cannot be due to electrostatic non-ideality, because such effects have been shown to be negligible by means of a comparison of non-electrolytic and electrolytic solutions (Part I, *J.*, 1950, 2473); and non-ideality effects due to solvation have already been taken into account. Therefore it must be concluded that the low ν-values are real, and that, in the more concentrated solutions, each molecule of ammonium hydrogen disulphate actually does produce an average of less than two solute particles. Since it is not conceivable that the ammonium ion undergoes any change, we have to accept the alternative that two or more hydrogen disulphate ions interact in some way to give a more complex multiple charged ion, perhaps together with a solvent molecule. The simplest possibility involves the transfer of a sulphur trioxide molecule from one hydrogen disulphate ion to another, followed by the transfer of a proton from the formed hydrogen trisulphate ion (which is expected to be an acid of considerable strength—cf. Section 1.2 to the basic hydrogen sulphate ion :

$$\left.\begin{aligned} 2HS_2O_7^- &= HS_3O_{10}^- + HSO_4^- \\ HS_3O_{10}^- + HSO_4^- &= S_3O_{10}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Any incompleteness in the second stage of this process constitutes a solvolysis of the trisulphate ion, with the formation of such extra hydrogen sulphate ion as that to which reference was made above in connexion with the probable over-correction of the freezing points for the suppression of solvent dissociation.

The next simplest possibility involves the formation of the ions of tetrasulphuric acid from three hydrogen disulphate ions :

$$\left.\begin{aligned} 3HS_2O_7^- &= HS_4O_{13}^- + 2HSO_4^- \\ HS_4O_{13}^- + HSO_4^- &= S_4O_{13}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Further condensations after this pattern are in principle possible. We cannot yet analyse the processes in detail, but we must, for reasons based on the mass law, expect all such equilibria to shift in the direction favouring anions of higher polysulphuric acids as the stoicheiometric concentration of ammonium hydrogen disulphate is increased. Furthermore, we must expect, not only on account of the mass law which alone would require the result, but also because higher polysulphuric acids should be stronger acids than lower, especially with respect to second stages of dissociation, that there will be a general shift towards doubly charged anions as the stoicheiometric concentration of the amonium salt is increased. This, then, is the qualitative interpretation of the observed fall in the ν-factors with increasing concentrations of the salt.

We can now proceed to the evaluation of the solvolysis constant of the hydrogen disulphate ion. From the above discussion it is clear that, if we could employ ν″ values for such low concentrations that trisulphates and higher polysulphate were completely absent, we could determine the solvolysis constant from the ordinary mass-law expression, which can thus be written in the form of a limit, as follows, Φ_0 being simply an abbreviation for the explicit function on the right :

$$K_s(HS_2O_7^-) = \operatorname{Lim}_{\Delta m \to 0} (\Phi_0) = \operatorname{Lim}_{\Delta m \to 0} \{(\nu'' - 2)^2 \Delta m/(3 - \nu'')\}$$

In this formula ν″ is a function of Δm, the molality of the ammonium hydrogen disulphate; and it rises to 3 as Δm approaches zero, independently of any effect due to higher polysulphuric acids. Thus ν″ is not a suitable quantity for extrapolation to low concentrations on the basis of the data of Table II. Even the expression Φ_0 is not convenient for extrapolation, owing to the strong variation in this function, which is caused by the disturbance due to the higher acids. However, we can derive an expression more suitable for extrapolation by enquiring in what form the deviation of the function from constancy should first appear when, on proceeding from very dilute towards slightly more concentrated solutions, the ions of the higher polysulphuric acids begin to be formed.

The first disturbance to ν″, which should arise from the formation of the higher acids, has reference to the equilibrium

$$2HS_2O_7^- = S_3O_{10}^{--} + H_2SO_4$$

the constant of which, $[S_3O_{10}^{--}]/[HS_2O_7^-]^2$, we will call α. Supposing the conversion to be

small, the fraction of ammonium hydrogen disulphate converted into the doubly charged ion will be $2\alpha\Delta m$, and this will be equal to twice that lowering of ν'' which results from the establishment of the equilibrium. Hence the initial deviation of Φ_k is to be corrected by simply adding $\alpha\Delta m$ to ν''. Accordingly, we may set up the following more general expression for the solvolysis constant

$$K_k(HS_2O_7^-) = \lim_{\Delta m \to 0} (\Phi_\alpha) = \lim_{\Delta m \to 0} \{(\nu'' + \alpha\Delta m - 2)^k \Delta m/(3 - \nu'' - \alpha\Delta m)\}$$

With a correct choice of α, the genalised function Φ_α should remain constant up to concentrations at which either the conversion into the trisulphate ion is no longer small, or the formation of the tetrasulphate ion is beginning to become important. All choices of α should lead to the same limit, provided that the function varies slowly enough at low concentrations to be extrapolated. In Table III values of Φ_α are given which are calculated from the data of Table II for three different choices of α. All three functions, despite their strong divergence at the higher concentrations, extrapolate to the same low-concentration limit of $10^2K_k = 8{\cdot}0$ g.-mol. kg.$^{-1}$.

TABLE III.

Values of Φ_α leading to the solvolysis constant of the hydrogen disulphate ion.

Δm.	ν''.	$10^2\Phi_{0\cdot2}$.	$10^2\Phi_{0\cdot3}$.	$10^2\Phi_{0\cdot4}$.	Δm.	ν''.	$10^2\Phi_{0\cdot2}$.	$10^2\Phi_{0\cdot3}$.	$10^2\Phi_{0\cdot4}$.
0·115	2·14	6·4	7·9	9·7	0·230	1·99	4·5	8·0	14·2
0·144	2·10	5·8	8·0	11·0	0·220	1·98	3·0	5·7	11·0
0·158	2·08	6·3	8·9	12·1	0·389	1·82	1·0	5·2	21·2
0·168	2·07	6·8	9·5	12·5	0·398	1·82	1·2	5·4	21·4
0·202	2·02	4·7	8·1	12·4					

Obviously the equilibrium constant α is in the neighbourhood of 0·8 g.-mol.$^{-1}$ kg. This means that, in a 0·1 molal solution of ammonium hydrogen disulphate, about 14% of the salt is converted into 7 mols. % of ammonium trisulphate.

(2.2) *Initial Effect of Ammonium Sulphate on the Freezing Point of Oleum.*—The presence of higher polysulphate ions in solutions of ammonium hydrogen disulphate implies the presence, along with disulphuric acid, of higher polysulphuric acids in oleum; for the production, by the addition of ammonium sulphate to oleum, of the various anions represented in equations (8) and (9), can evidently be represented as a progressive removal of protons, by the basic hydrogen sulphate ion, from molecules of the appropriate polysulphuric acids, *e.g.*,

$$\left.\begin{aligned} H_2S_3O_{10} + HSO_4^- &= HS_3O_{10}^- + H_2SO_4 \\ HS_3O_{10}^- + HSO_4^- &= S_3O_{10}^{--} + H_2SO_4 \end{aligned}\right\} \quad \ldots\ldots (10)$$

The anions being present, these equilibria must be set up, and hence the acids must be present, ionised or otherwise; for the question of the extent to which the anions are solvolysed is just that of the extent to which the acids are ionised.

These higher polysulphuric acids must participate in equilibria such as the following:

$$\left.\begin{aligned} 2H_2S_2O_7 &= H_2S_3O_{10} + H_2SO_4 \\ 3H_2S_2O_7 &= H_2S_4O_{13} + 2H_2SO_4 \end{aligned}\right\} \quad \ldots\ldots\ldots (11)$$

On account of the mass law, such equilibria must shift in the direction favouring higher polysulphuric acids in stronger oleums.

It is possible on these ground to understand the peculiar effect of small amounts of added ammonium sulphate on the freezing points of oleums of different strengths. Reference to Fig. 1 (p. 2521) shows that all the ammonium sulphate curves start towards the left with a smaller downward slope than that which they acquire after a considerable quantity of ammonium sulphate has been added; and also that this reduced initial downward slope becomes still smaller as the strength of the original oleum becomes greater, even changing sign in the example of the strongest of the oleums, the ammonium sulphate curve for which rises initially.

The interpretation is as follows. We assume it to be a sufficient description of the limiting situation in very dilute oleum that only disulphuric acid and its ions are present. In this case the first effect of added ammonium sulphate will be to destroy the cation of the ionised acid, and thus to replace it by ammonium ion; and then, in order to restore the ionic equilibrium, some more molecular disulphuric acid will become ionised, a process which will increase the number of solute particles. In more concentrated oleum, a certain amount of trisulphuric acid will be present; and, as this is expected to be a stronger acid than disulphuric acid, it will tend to be destroyed first by the basic hydrogen sulphate ion. The effect of added ammonium sulphate

on trisulphuric acid and its ions will be exactly as described for disulphuric acid, except that the loss of molecular trisulphuric acid by the ionisation, which it undergoes in order to replace its destroyed cation, will be restored from the pool of disulphuric acid, in accordance with the first of equations (11). This last step involves a disappearance of solute particles, and all the steps together lead to a reduced increase, up to the limit of no net change in the total number of solute particles. Thus, if the first-added ammonium sulphate should act only on the trisulphuric acid, the freezing-point curve would start horizontally, acquiring its normal downward slope at a later stage, when the trisulphuric acid had been " neutralised " and only disulphuric acid remained in a free condition. In this way we can qualitatively account for all the mentioned effects, except the initial rise of the freezing-point curve which is observed in the case of the strongest of the oleums. An actual rise in the curve cannot be explained by any of the possible reactions of trisulphuric acid.

However, we may suppose that the most concentrated of the oleums will contain appreciable amounts of tetrasulphuric acid; and that this, as the strongest acid present, will tend to be destroyed first by added ammonium sulphate. The mechanism of its destruction will be just as for trisulphuric acid, except that, since the last step is the restoration of molecular tetrasulphuric acid according to the second of equations (11) the loss of solute particles in this step will be twice as great as before. The over-all effect of the neutralisation of tetrasulphuric acid can therefore be to reduce the number of solute particles, and thus to produce an initially rising freezing-point curve. Tetrasulphuric acid is the lowest polysulphuric acid that can produce this effect, the observation of which provides clear evidence of the existence of the acid.

The presence of these higher acids in oleum makes it necessary to reconsider the provisional estimate given in Part II (*J.*, 1950, 2493) of the acidity constant K_a of disulphuric acid. The estimation was based on the measured ν-factors of the acid, the excess of ν over unity being ascribed to the first stage of ionisation of the acid. However, the formation and ionisation of the higher polysulphuric acids must disturb both the factors ν and the derived constant K_a. The observed increase of K_a with increase of concentration (cf. Part II, Table V) indicates that the effect of the higher polysulphuric acids is to increase ν, and therefore to increase the apparent K_a of disulphuric acid. This seems very reasonable; for the higher polysulphuric acids are likely to be stronger acids than disulphuric acid in both stages of ionisation, but especially in the second stage; and therefore the higher acids might be almost completely ionised as to the first stage, and largely ionised with respect to the second, when disulphuric acid is still only partly ionised with respect to the first stage. One way of eliminating the disturbing effect of the higher acids would be to extrapolate the apparent K_a of disulphuric acid to the limit of low oleum concentrations, *i.e.*, to the limit of low proportions of the higher poly-acids among the total poly-acids. The mean " apparent " K_a, called K_a', was given in Part II as 0·028 g.-mol. kg.$^{-1}$. It is possible to make an extrapolation of the kind suggested on the basis of the data of which a sample is recorded in Part II. The result is to show that the true K_a of disulphuric acid is in the neighbourhood of 0·020 g.-mol. kg.$^{-1}$. Confirmation of this value will be offered in Section 4.1.

(2.3) *Effect of Ammonium Sulphate on the Freezing Point of Solutions of Ammonium Hydrogen Disulphate.*—We proceed now to the discussion of the slopes at the other ends of the freezing-point curves for added ammonium sulphate. Three of these curves (Expts. No. 10, 104, and 105) have been carried over to the basic side of the neutral line (cf. Fig. 1, p. 2521). On the neutral line the composition is that of a solution of ammonium hydrogen disulphate in sulphuric acid. At points to the left the composition may be expressed in terms of the concentration of the basic solute, ammonium hydrogen sulphate, which has been introduced into the solution of the " neutral " salt.

The freezing points of the most basic solutions measured in these experiments, together with the derived freezing-point depressions, and ν-factors, are given in Table IV. The depressions, θ', are calculated with reference to the freezing point, 10·62°, which pure sulphuric acid would have if it were not self-dissociated. The correction of these depressions to allow for residual solvent dissociation was made as is described in connexion with Table II. The corrected values are called $\Delta\theta''$. The ν-factors are calculated by means of equation (4) of Part I (*J.*, 1950, 2473), with the insertion $z_3 = 1$, $\nu_3 = 2$, and $m_3 = 0$, in the correction factor, the first of these substitutions taking account of the solvation of the ammonium salts (cf. Part I). These ν-factors, called ν'' in the Table, refer to total solutes, ammonium hydrogen disulphate and ammonium hydrogen sulphate. For comparison, Table IV contains the values of ν for ammonium hydrogen disulphate alone, as measured in solutions which are the same except for the absence of the excess of ammonium hydrogen sulphate (cf. Table II).

TABLE IV.

Freezing points of solutions of mixtures of ammonium hydrogen disulphate and ammonium hydrogen sulphate.

Expt. no.	F. p. (° c.).	Depression. $\Delta\theta$.	Depression. $\Delta\theta'$.	Molalities. $AmHS_2O_7$.	Molalities. $AmHSO_4$.	Molalities. Total.	Overall ν'.	ν $(AmHS_2O_7)$.
104	7·949	2·67°	2·64°	0·167	0·064	0·231	1·90	2·07
105	7·697	2·92	2·90	0·158	0·100	0·258	1·86	2·08
10	7·153	3·47	3·45	0·220	0·102	0·322	1·78	1·98

In Section 2.1 it was shown that the ν-factor for ammonium hydrogen disulphate arises partly from its ionisation, which alone would give the value 2, partly from the accompanying solvolysis of the hydrogen disulphate ion, which tends to raise the value, and partly from the simultaneous conversion into higher polysulphate ions, which tends to reduce the figure. Table IV shows that the addition of ammonium hydrogen sulphate considerably reduces the over-all ν-value; and this must mean that the hydrogen sulphate ion combines with the hydrogen disulphate ion, or with its conversion products, in some way which reduces the total number of solute particles. The possibilities are all of one type, *viz.*

$$\left.\begin{aligned} HSO_4^- + HS_2O_7^- &= S_2O_7^{--} + H_2SO_4 \\ HSO_4^- + HS_2O_{10}^- &= S_2O_{10}^{--} + H_2SO_4 \\ HSO_4^- + HS_4O_{13}^- &= S_4O_{13}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

A further indication of the extent to which such processes take place may be obtained by computing the ν-factors for the last increment of ammonium hydrogen sulphate, employing for the purpose the observations on the two most basic solutions used in each experiment. The results of these calculations are in Table V. The correction for the decrease of residual self-dissociation is here only approximate, and hence ν is given to two figures only.

TABLE V.

Values of the ν-factor for ammonium hydrogen sulphate in solutions of this salt and of ammonium hydrogen disulphate in sulphuric acid.

Expt. no.	F. p. (° c.).	$\Delta\theta$ (corr.).	Molalities. $AmHS_2O_7$.	Molalities. $AmHSO_4$.	Δm $(AmHSO_4)$.	ν $(AmHSO_4)$.
105	8·030 7·697	0·35°	0·158	0·0655 0·1004	0·0349	1·7
104	8·242 7·949	0·32	0·167	0·0303 0·0638	0·0335	1·6
10	7·478 7·153	0·35	0·220	0·0630 0·1020	0·0390	1·5

It is immediately apparent that a large proportion, *e.g.*, one-half, of the increment of hydrogen sulphate ions becomes consumed in the reactions represented by equations (12). The most interesting point, however, is that not nearly the whole of the hydrogen sulphate ion is thus consumed. We expect theoretically (Section 1.2) that the hydrogen trisulphate and higher hydrogen polysulphate ions are rather strong acids, and we have experimental indications (Section 2) that this is so. It is therefore likely that these ions, $HS_3O_{10}^-$, $HS_4O_{13}^-$, etc., would yield up their protons rather completely to the basic hydrogen sulphate ion in the reactions indicated by equations (12). Indeed, it seems probable that they will have largely done so, before the introduction of the particular increment of hydrogen sulphate ion under consideration. Therefore the fact that this increment is only partly destroyed must mean that the next acid from which it could obtain protons, *viz.*, the hydrogen disulphate ion, $HS_2O_7^-$, which will still be present in substantial quantity, is a very weak acid.

This conclusion is confirmed in Section 3.1; and it agrees with the assumption, made at the outset of Section 2.1, that, since the hydrogen disulphate ion transfers protons only in a limited way to the basic hydrogen sulphate ion, it will be unable to transfer them to sulphuric acid molecules to any extent of which count need be taken in relation to the totality of proton transfers occurring on the acid side of the neutral line of Fig. 1. This conclusion is otherwise expressed by the statement that the second dissociation constant of disulphuric acid is much

smaller than the first—in contrast to the situation apparently obtaining in the higher polysulphuric acids (cf. Section 1.2).

(3) *Effect of Water on the Freezing Points of Solutions of Ammonium Sulphate in Oleums. Reactions involved in the Titration of Oleum Solutions with Water.*

(3.1) *Effect of Water on the Freezing Points of Solutions of Ammonium Sulphate in Oleums.*—When successive amounts of water are added to a solution having the composition of a solution of ammonium hydrogen disulphate in sulphuric acid, the freezing point at first rises, then passes through a maximum, and then descends. Let us first consider the initial rise in the freezing point, *e.g.*, the section *a*—*b* of the curve of Expt. No. 106, shown in Fig. 1.

At *a*, on the neutral line, the solute has the composition of ammonium hydrogen disulphate. We should expect the added water to replace the hydrogen disulphate ion by the hydrogen sulphate ion, a process which should not change the freezing point:

$$HS_2O_7^- + H_2O = HSO_4^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

However, at *a*, as we have seen, the ν-factor rises above 2·00, essentially owing to solvolysis of the hydrogen disulphate ion:

$$HS_2O_7^- + H_2SO_4 = H_2S_2O_7 + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Nevertheless, the precise value of ν is affected by two disturbances, one due to incomplete repression of the autoprotolysis of the solvent, and the other due to the formation of some trisulphate, or other higher polysulphate, anions. The water added, and the hydrogen sulphate ion formed from it, should diminish both disturbances; and, what is more important, it should considerably repress the main reaction (14). Essentially on this last account the ν-factor should fall, and the freezing point should rise.

At the freezing-point maximum *b*, it may be assumed that the solvolytic reaction (14) has been completely repressed, and that disulphuric acid molecules are absent. Since the only solutes should now be ammonium hydrogen disulphate and ammonium hydrogen sulphate, the ν-factor should have fallen to 2·00. Actually the freezing point rises higher than would be calculated on this basis, the ν-factor having fallen to 1·95; and still smaller ν-factors are obtained from the measurements on the more concentrated solutions used in the other experiments on the effect of added water. This is indicated in Table VI, the ν-factors in which are calculated from freezing-point depressions reckoned with reference to the theoretical freezing point of non-dissociated sulphuric acid, 10·62°, and then corrected as usual for residual self-dissociation.

TABLE VI.

Values of the ν-factor at the maximum freezing point obtained by adding water to solutions of ammonium sulphate in oleums.

Expt.	F. p. (° c.).	$\Delta\theta$ (corr.).	Molality.*	ν-Factors.
106	9·23	1·34°	0·115	1·95
12	8·20	2·29	0·202	1·89
11	6·52	4·09	0·389	1·75

* Molality of ammonium ion, or *equivalent*-molality of total singly and doubly charged anions.

These reductions in the ν-factors must mean that ammonium hydrogen disulphate and ammonium hydrogen sulphate are not the only solutes at the freezing-point maximum; and, indeed, that these substances have interacted, to produce a net loss of solute particles, as was discussed in Section 2.3:

$$HS_2O_7^- + HSO_4^- = S_2O_7^{--} + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Since the hydrogen sulphate ion is the strongest base that can occur in quantity in solvent sulphuric acid, the circumstance that, in the presence of approximately equivalent amounts of the two ions, reaction (15) does not go nearly to completion is a clear indication of the weakness of the hydrogen disulphate ion as an acid in this solvent.

The decrease of the ν-factor from 1·95 to 1·75 with increasing concentration is too great to be attributed solely to a mass-action effect on equilibrium (15), and it must therefore indicate the presence of higher polysulphate ions in these solutions. It has been shown that, at the neutral line, the more concentrated solutions contain considerable amounts of singly and doubly

charged higher polysulphate ions : added water will desulphate these according to reactions, such as (16), which do not change the freezing point :

$$\left.\begin{aligned} HS_2O_{10}^- + H_2O &= HS_2O_7^- + H_2SO_4 \\ S_2O_{10}^{--} + H_2O &= S_2O_7^{--} + H_2SO_4 \\ HS_4O_{13}^- + H_2O &= HS_2O_{10}^- + H_2SO_4 \\ S_4O_{13}^{--} + H_2O &= S_2O_{10}^{--} + H_2SO_4 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Reference to Fig. 1 will show that the rise in freezing point from the neutral line to the maximum, on adding water, is relatively small in the most concentrated solution; and this indicates that the reactions occurring on the addition of water are, in fact, mainly (13) and (16). However, the large fall of ν-factor with increasing concentration indicates that reactions (16) are not complete at the maximum, and that these solutions contain, therefore, in addition to the hydrogen disulphate and normal disulphate ions, a certain quantity of doubly charged higher polysulphate ions.

If one continues to add water, passing beyond the freezing-point maximum until a point is reached, such as *c* in Fig. 1, at which the total amount of added water is stoicheiometrically sufficient to complete reaction (13), then disulphuric acid and both its anions should have been destroyed, as well as all higher polysulphuric acids and their anions. Thus the only surviving solute should be ammonium hydrogen sulphate; and now the ν-factor really should be 2·00.

The result of this test is given in Table VII. The freezing-point depressions $\Delta\theta'$ are calculated with reference to the theoretical freezing point, 10·62°, of the non-dissociated solvent. The depressions $\Delta\theta''$ are corrected as usual for the repression of solvent dissociation. The resulting ν-values are labelled ν″. They are equivalent to a confirmation of the value, 10·52°, deduced in Part I (*J.*, 1950, 2473) for the freezing point of self-dehydrated, but not autoprotolysed sulphuric acid. In these solutions, and especially in the more concentrated ones, the solvent is very approximately in this condition. If we calculate that solvent freezing point from which depressions should be reckoned in order that they shall give a value of exactly 2·00 to the ν-factor of ammonium hydrogen sulphate, the results are 10·53°, 10·51°, and 10·52° for Expts. No. 106, 12, and 11, respectively (mean 10·52°).

TABLE VII.

Freezing points and ν-factors of solutions of ammonium hydrogen sulphate.

			Depression.		
Expt. no.	F. p. (° c.).	Molality.	$\Delta\theta'$.	$\Delta\theta''$.	ν″.
106	9·16	0·115	1·46°	1·34°	1·95
12	8·09	0·202	2·53	2·42	2·01
11	5·89	0·389	4·73	4·63	2·00

If one still continues to add water, thus passing beyond points such as *c*, for which the solute is ammonium hydrogen sulphate, the freezing-point curves descend rapidly. This is because the extra water becomes ionised according to the equation

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

As is established in Part II (*J.*, 1950, 2493) reaction (17) is not quite complete, being governed by a definite equilibrium constant.

In two experiments the measurements were made by which ν-factors can be calculated for an increment of added water over a part of the freezing-point curve lying wholly beyond the point for which the solute is ammonium hydrogen sulphate. Even in these solutions ionic self-dehydration and autoprotolysis of the solvent are not fully repressed, and a correction for the further repression effected by the increments of water is applied in reckoning the freezing-point depressions due to the water. The derived ν-factors for the increments of water are given in the penultimate column of Table VIII. They ought to be equal to those ν-factors for water in the presence of hydrogen sulphate ions, which can be calculated from the basicity constant for water, as determined in Part II, by the methods (if they are still accurate at the highest of the concentrations now employed) already illustrated in other connexions in Part III (*J.*, 1950, 2504). The ν-factors thus computed are entered in the last column of Table VIII.

(3.2) *Reactions involved in the Titration of Oleum Solutions with Water.*—Brand (*J.*, 1946, 585, 880) has developed a method for the estimation of the stoicheiometric concentration of sulphur trioxide in solvent sulphuric acid by titration with water until, under specified conditions

TABLE VIII.

Values of the ν-factor for water in the presence of ammonium hydrogen sulphate.

			Molalities.			ν (H_2O).	
Expt. no.	F. p. (° c.).	$\Delta\theta$ (corr.).	$AmHSO_4$.	H_2O.	Δm (H_2O).	Found.	Calc.
106	8·933 8·386	0·550°	0·1145	0·0287 0·0777	0·0490	1·62	1·81
12	7·877 7·273	0·605	0·202	0·0263 0·0814	0·0551	1·80	1·74

and at a stated temperature, fuming ceases to be visible; and he has applied this technique in order to determine the extent to which certain substances, when dissolved in oleum, reduce the amount of sulphur trioxide which can be titrated in this way. Potassium hydrogen sulphate was found to reduce the titratable sulphur trioxide by 0·5 mol. per mol. of added salt; and other solutes were found to reduce the sulphur trioxide by amounts, which accorded with their known modes of ionisation, if the assumption was made that each mol. of formed hydrogen sulphate ion always removed 0·5 mol. of sulphur trioxide. Brand pointed out that fuming must indicate the presence of non-ionised disulphuric acid; and he offered a hypothesis which attributes stoicheiometric significance to the factor 0·5, the suggestion being that molecular disulphuric acid is not wholly destroyed until the second stage of its ionic dissociation, as well as the first, is substantially complete, two hydrogen sulphate ions being required for each molecule of disulphuric acid thus converted:

$$H_2S_2O_7 + 2HSO_4^- = S_2O_7^{--} + 2H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The hypothesis would imply that the acidity of the hydrogen disulphate ion is not much less than that of the disulphuric acid molecule, contrary to conclusions reached in Sections 2.3 and 3.1.

Let us consider what happens when, say, potassium hydrogen sulphate is added to an oleum, and the excess of sulphur trioxide is titrated with water. For simplicity in a preliminary description, we shall ignore the formation of any polysulphates more complex than disulphates. The potassium hydrogen sulphate can be regarded as being first converted into potassium hydrogen disulphate; and, if the stoicheiometric excess of sulphur trioxide is removed by the addition of water, the total solute will then have the composition of potassium hydrogen disulphate. However, the solution will still contain a substantial proportion of molecular disulphuric acid, and therefore will still fume, because of the incompleteness of the first stage of ionisation of disulphuric acid, or, in other words, because of the proved solvolysis (Section 2.1) of the hydrogen disulphate ion in the following balanced reaction:

$$H_2S_2O_7 + HSO_4^- = HS_2O_7^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Therefore more water must be added to stop fuming; and, since we have the relation $[H_2S_2O_7] = K_b[HS_2O_7^-]/[HSO_4^-]$, with $K_b = 0{\cdot}008$ molal, an upper limit can be set to the amount of extra water needed. It cannot be as much as would convert all the hydrogen disulphate ion into hydrogen sulphate ion, and thus reduce the ratio $[HS_2O_7^-]/[HSO_4^-]$ to zero; for that would imply a titration technique of infinite sensitivity. Brand's results mean that fuming ceases to be visible, under his conditions, when enough extra water has been added to convert about one-half of the hydrogen disulphate ion into hydrogen sulphate ion, thus reducing the ratio $[HS_2O_7^-]/[HSO_4^-]$ to about unity, and therefore the concentration of molecular disulphuric acid to about 0·008 mol.

It will be noted that the above description does not assume that the hydrogen disulphate and hydrogen sulphate ions must necessarily be produced in equal amounts because in order to stop fuming they have to undergo the completed reaction

$$HS_2O_7^- + HSO_4^- = S_2O_7^{--} + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

a process which, with (19), constitutes Brand's reaction (18). The interpretation based on the solvolysis of the hydrogen disulphate ion makes the factor 0·5 a chance result, dependent on the magnitude of the solvolysis constant in relation to the sensitivity of the titration method under the conditions (particularly the temperature) chosen for its operation. This does not imply that reaction (20) does not proceed at all: it was shown in Section 3.1 that it does take place to a limited extent. But the occurrence of any substantial solvolysis according to equation (19)—and it was shown in Section 2.1 that such solvolysis is substantial—is enough to destroy the stoicheiometric significance of the factor 0·5.

A very slight extension of the discussion already given of Expts. No. 11, 12, and 106 establishes these conclusions. At point *a* in Fig. 1, some molecular disulphuric acid is present, and this is why the point lies as low as it does; but towards *b* the disulphuric acid becomes consumed by the increasing concentration of hydrogen sulphate ions, and so the freezing point rises. At the freezing-point maximum *b*, the molecular disulphuric acid should have been destroyed; and at this point the composition corresponds approximately (but not exactly) to equivalent proportions of ammonium hydrogen sulphate and ammonium hydrogen disulphate, and therefore to the end-point of the water titration. The datum which shows quite clearly that, at and near the freezing-point maximum *b*, and therefore at the end-point of the water titration, the solute is not normal ammonium disulphate, formed in a completed reaction (20), is that the *v*-factor is not 1·5. It is 1·95; and the defect below 2·00 measures the degree of incursion of reaction (20).

The neglect of the higher polysulphates in this discussion is probably justified for dilute solutions, such as apply to Expt. 106, but not for the more concentrated solutions, *e.g.*, of Expt. 11. The relatively small rise in the freezing point that occurs on the addition of water to more concentrated solutions of ammonium hydrogen disulphate has been explained in Section 3.1 as being due to the occurrence of reactions (13) and (16). It was also pointed out that the higher polysulphate ions, originally present at the neutral line, are not completely destroyed by the addition of an amount of water sufficient to reach the freezing-point maximum (or the end-point of the water titration). Again, therefore, we find a fortuitous situation, inasmuch as the values of the various equilibrium constants, determining the relative amounts of polysulphate ions and non-ionised disulphuric acid, are such that the amount of non-ionised disulphuric acid is reduced to a quantity less than can be detected by the fuming property (*i.e.*, less than 0·008 molal) in a solution containing approximately equal concentrations of hydrogen sulphate and hydrogen disulphate ions.

(4) *Further Comments on the Species present in Sulphuric Acid and in Dilute Oleum.*

(4.1) *The Self-dissociation Equilibria of Sulphuric Acid.*—The present analysis of the dissociation equilibria of sulphuric acid is dependent on our being able to estimate three quantities, *viz.*, the total concentration of the dissociation products, the solvolysis constant of the hydrogen disulphate ion, and the acidity constant of disulphuric acid. These quantities have to be combined in the following way. Since the product of the acidity constant of any acid and the solvolysis constant of the corresponding anion in any solvent, will always give the autoprotolysis constant of the solvent, the acidity constant of disulphuric acid, and the solvolysis constant of the hydrogen disulphate ion, in sulphuric acid, will allow us to compute the autoprotolysis constant of sulphuric acid. Thus one can obtain the concentrations of each of the autoprotolytic ions; and, in so far as it may be found that these concentrations are not great enough to make up the estimated concentration of total dissociation products, a balance will remain which can be assigned to the products of the ionic self-dehydration.

The total concentration of dissociation products is the best known of the three required quantities. It was determined in Part II to be 0·043 molal, *i.e.*, enough to lower the freezing point of the solvent by 0·26°.

In consequence of the work described in Section 2.1, the value of the solvolysis constant of the hydrogen disulphate ion is taken to be as follows :

$$K_b(HS_2O_7^-) = [H_2S_2O_7][HSO_4^-]/[HS_2O_7^-] = 0{\cdot}0080 \text{ g.-mol. kg.}^{-1}$$

From this value of K_b, and the acidity constant of disulphuric acid, as deduced in Section 2.2 of this paper, on the basis of work reported in Part II, *viz.*,

$$K_a H_2S_2O_7 = [H_2SO_4^+][HS_2O_7^-]/[H_2S_2O_7] = 0{\cdot}020 \text{ g.-mol. kg.}^{-1},$$

the ionic product for autoprotolysis may be calculated. From this, and the total concentration of dissociation products, one may compute the ionic product for self-dehydration. The results are as follows :

$$K_{sp} = [H_2SO_4^+][HSO_4^-] = 0{\cdot}00016 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$
$$K_{sd} = [H_3O^+][HS_2O_7^-] = 0{\cdot}00008 \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

These values agree closely with those, noted in Section 1.1 of this paper, which were derived from data given in Parts I and II.

(4.2) *Collateral Evidence of the Existence of Higher Polysulphuric Acids.*—In this paper the existence has been indicated of a number of polysulphuric acids higher than disulphuric acid;

and specific evidence has been presented that at least trisulphuric acid and tetrasulphuric acid are present in appreciable quantities in dilute, or moderately dilute, oleum. Further support for these conclusions is afforded by Raman spectroscopic evidence, as is described by Millen in an accompanying paper (*J.*, 1950, paper no. 507). It therefore seems natural to consider whether any collateral evidence of the existence of these higher acids can be obtained, either from the isolation of salts or derivatives, or from the proved existence of analogously constituted acids.

When alkali-metal sulphates are heated with sulphur trioxide at temperatures between 100° and 300°, and the excess of sulphur trioxide is distilled off, a stable solid remains, which is invariably found to be the disulphate, $M_2S_2O_7$. This might mean only that the metallic trisulphates and tetrasulphates are unstable to heat, and not that they cannot exist at any temperature.

On the other hand, it is certain that both nitrosonium and nitronium salts, not only of disulphuric acid, but also of some of the higher polysulphuric acids, can be prepared. Nitrosonium disulphate, $(NO)_2S_2O_7$, is well known. When heated, it begins to decompose at about 100°, giving off oxides of nitrogen; and near 300° the material boils, and a white solid collects on the cooler surfaces. There has been some dispute about the composition of this solid. According to Jones, Price, and Webb (*J.*, 1929, 312) it has the composition $2N_2O_3,5SO_3$: as a molecular formula this seems unlikely; but it might indicate a mixture of the original disulphate with the trisulphate, $(NO)_2S_3O_{10}$. However, according to Manchot and Schmidt (*Ber.*, 1929, **62**, 126), the white solid has the composition of nitrosonium tetrasulphate, $(NO)_2S_4O_{13}$. What seems clear is that the material possesses a higher sulphur-to-nitrogen ratio than does the original disulphate, and that therefore it probably contains a higher polysulphate. The evidence concerning nitronium salts is more definite. In an accompanying paper, Goddard, Hughes, and Ingold describe both of the nitronium disulphates, $(NO_2)HS_2O_7$ and $(NO_2)_2S_2O_7$. They also describe nitronium trisulphate, $(NO_2)_2S_3O_{10}$, which they found to be stable up to temperatures above 100°. They attempted, but failed, to prepare nitronium tetrasulphate.

Next, by arguments of analogy, the thesis may be developed that the tendency to the formation of higher poly-acids $H_2O(XO_3)_n$, which is so marked a feature of the chemistry of molybdenum and tungsten, is already developed to some extent in that of sulphur, and that the phenomenon can be traced back through the chemistry of the intermediate elements, selenium and chromium, as well as, in the other direction, to that of uranium.

Diselenic acid, $H_2Se_2O_7$, has never been prepared, presumably because selenium trioxide is very difficult to prepare, and has never been obtained in a state of purity. However, Goddard, Hughes, and Ingold showed (*loc. cit.*) that nitronium salts of diselenic acid exist, $(NO_2)HSe_2O_7$, or $(NO_2)_2Se_2O_7$, or both, although, here again, they were not able to obtain a pure individual. Meyer and Stateczny (*Z. anorg. Chem.*, 1922, **121**, 1) studied the phase diagram of the system H_2SeO_4–SO_3, and observed the formation of two stable solid compounds, selenatosulphuric acid, H_2SSeO_7, and selenatodisulphuric acid, $H_2S_2SeO_{10}$. The latter is clearly an analogue of trisulphuric acid. Although the authors do not mention the point, their freezing-point curve suggests the existence of a third compound, probably selenatotrisulphuric acid, $H_2S_3SeO_{13}$, the analogue of tetrasulphuric acid. Selenatosulphuric acid melts at 6·6°, and selenatodisulphuric acid at 20°; both compounds fume in air. Salts of selenatosulphuric acid have been prepared, but not salts of selenatodisulphuric acid.

Neither dichromic acid, $H_2Cr_2O_7$, nor any of the higher polychromic acids, have yet been prepared in the pure condition, owing to their tendency towards self-dehydration. But the salts, $M_2Cr_2O_7$, of dichromic acid are familiar substances, and a number of metallic trichromates and tetrachromates, $M_2Cr_3O_{10}$ and $M_2Cr_4O_{13}$, are known. On the other hand, two hetero-di-acids containing chromium have been obtained, not only as salts, but also in the free state. They are chromatosulphuric acid, and chromatoselenic acid, H_2SCrO_7 and H_2SeCrO_7 (Gilbert, Buckley, and Masson, *J.*, 1922, **121**, 1934; Meyer and Stateczny, *loc. cit.*).

It would thus appear that the present work extends to sulphur a property which is somewhat general in the chemistry of Group VI elements.

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501. *Cryoscopic Measurements in Sulphuric Acid. Part V. Ionisation of Nitric Acid in Sulphuric Oleum.*

By R. J. Gillespie and J. Graham.

When nitric acid is added in increasing quantities to oleum, the freezing point behaves as is shown in Fig. 1, p. 2534. The freezing points of the original oleums lie on the curve limiting the diagram towards the right. The freezing-point curves for added nitric acid run towards the left, rising, passing through maxima, and then falling with increasing gradient.

The main reactions, apart from proton-transfers, are as follows: first, nitric acid desulphates half the disulphuric acid, producing essentially nitronium hydrogen disulphate:

$$HNO_3 + 2H_2S_2O_7 = NO_2^+ + HS_2O_7^- + 2H_2SO_4$$

and then, it desulphates the remainder, now present mainly as the hydrogen disulphate ion, to give nitronium hydrogen sulphate:

$$HNO_3 + HS_2O_7^- = NO_2^+ + 2HSO_4^-$$

The accompanying proton-transfer processes are as follows. Initially the disulphuric acid is partly ionised as an acid. The first effect of the developing hydrogen disulphate ion is to suppress this ionisation: thus the maximum of the freezing-point curve is reached. Then, as the free disulphuric acid becomes consumed, the hydrogen disulphate ion undergoes some solvolysis: here the freezing point begins to fall. At a later stage, the developing hydrogen sulphate ion partly deprotonates the hydrogen disulphate ion, to form some normal disulphate ion, which is the last form in which disulphuric acid resists desulphation: these processes steepen the fall of the freezing point.

Accompanying this main series of desulphation and deprotonation processes, a minor series must occur, consisting of the desulphation and deprotonation of the small amounts of higher polysulphuric acids originally present in the oleum.

The ν-factors of nitronium hydrogen disulphate and of nitronium hydrogen sulphate are extracted from the results. They agree well with the ν-factors of ammonium hydrogen disulphate and ammonium hydrogen sulphate, respectively. The result for nitronium hydrogen sulphate confirms the analysis, given in Part IV, of the self-dissociation processes of sulphuric acid.

(1) *Preliminary Consideration of the Ionisation of Nitric Acid in Dilute Oleum.*—The work to be reported has reference to the effect of added nitric acid on the freezing points of oleum solvents. It therefore extends the experiments described in Part III (*J.*, 1950, 2504) on the effect of nitric acid on the freezing point of slightly aqueous sulphuric acid. These experiments showed that nitric acid ionises in solvent sulphuric acid according to the following approximate equation:

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The same work also showed that a more exact treatment of this process required separate consideration of the following reaction-stages, of which the first proceeds to completion in a large excess of sulphuric acid, whilst the second is appreciably incomplete:

$$\left.\begin{aligned} HNO_3 + H_2SO_4 &= NO_2^+ + HSO_4^- + H_2O \\ H_2O + H_2SO_4 &= H_3O^+ + HSO_4^- \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

A detailed study of the second of these reactions, in the absence of the complicating presence of the first, was described in Part II (*J.*, 1950, 2493), where the equilibrium constant of the process was determined, which was applied in Part III in a quantitative interpretation of freezing-point measurements on the basis of equations (2).

It was shown in Part II, and in more detail in Part IV (*J.*, 1950, 2516), that dilute oleum can be regarded essentially as a solution, in the sulphuric acid solvent, of disulphuric acid, which is an acid of moderate strength, partly ionising according to the equation

$$H_2S_2O_7 + H_2SO_4 = HS_2O_7^- + H_3SO_4^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Two of the products of the first of reactions (2) are expected to interact with disulphuric acid: for water will desulphate the acid; and the hydrogen sulphate ion, which is the strongest base that can exist in quantity in solvent sulphuric acid, will deprotonate it:

$$\left.\begin{aligned} H_2O + H_2S_2O_7 &= 2H_2SO_4 \\ HSO_4^- + H_2S_2O_7 &= H_2SO_4 + HS_2O_7^- \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It follows that in oleum solvents the primary ionisation process of nitric acid, represented

by the first of reactions (2), will be succeeded, not by the second of reactions (2), but by the two reactions (4). The over-all effect may be expressed thus:

$$HNO_3 + 2H_2S_2O_7 = NO_2^+ + HS_2O_7^- + 2H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

However, this again is only an approximate expression. The nitronium and hydrogen disulphate ions are quite inert towards each other, as is shown by the formation and stability of solid nitronium hydrogen disulphate (Goddard, Hughes, and Ingold, *J.*, 1950, paper no. 505); and the nitronium ion is quite stable in sulphuric acid (Part III). But the hydrogen disulphate ion is not inert towards sulphuric acid, by which it is reversibly solvolysed, as was shown in Part IV. In other words, of the two reactions (4), the first may be taken as complete, while the second is often a measurably balanced reaction. It is thus convenient to decompose equation (5) into the following two stages, of which the first is complete, whilst the second may be appreciably incomplete:

$$\left.\begin{aligned} HNO_3 + H_2S_2O_7 &= NO_2^+ + HSO_4^- + H_2SO_4 \\ HSO_4^- + H_2S_2O_7 &= H_2SO_4 + HS_2O_7^- \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

A study of the reversibility of the second of these reactions, in the absence of complications due to the first, was recorded in Part IV (*loc. cit.*), where an equilibrium constant for the reaction is given, which should be applicable in a quantitative interpretation of relevant freezing-point data on the basis of equations (6).

Even this description of the ionisation processes of nitric acid in oleum is not complete, inasmuch as account has still to be taken of the formation and ionisation of the higher polysulphuric acids, which, except in very dilute oleum, are present in appreciable proportion (Part IV). It seems certain that the higher polysulphuric acids are stronger acids than disulphuric acid, especially with respect to the second stage of acid dissociation; and thus the higher acids tend, much more than does disulphuric acid, to enter into a second stage of ionisation. It follows that added bases will tend to deprotonate the higher polysulphuric acids in preference to disulphuric acid, and will begin to produce from the former appreciable proportions of doubly charged higher polysulphate ions, while they are simultaneously producing from disulphuric acid mainly the singly charged hydrogen disulphate ion. Effects on the freezing point, due to the shifting of this system of equilibria, under the influence of added ammonium sulphate caused by base-forming solute, are described in Part IV, and are available for comparison with the analogous effects of the bases which are produced in the ionisation of nitric acid by the reactions already mentioned.

(2) *Effect of Nitric Acid on the Freezing Point of Oleum.*—This has been investigated by the general methods described in previous Parts of this series. The results of two experiments are reported in Table I. They are graphically represented in Fig. 1. In the table and the figure

TABLE I.

Freezing points of solutions of nitric acid in dilute oleum.

Weights (g.).					Weights (g.).				
Added HNO_3.	$H_2S_2O_7$.	H_2SO_4.	Molality $H_2S_2O_7$.	F. p. (° c.).	Added HNO_3.	$H_2S_2O_7$.	H_2SO_4.	Molality $H_2S_2O_7$.	F. p. (° c.).
Expt. No. 13 G.					Expt. No. 14 G.				
—	2·980	65·85	0·2545	8·633	—	2·060	63·64	0·2350	8·762
0·0943	2·477	66·14	0·2078	8·771	0·1585	1·764	64·13	0·1501	8·981
0·1109	1·820	66·49	0·1538	8·902	0·1809	1·049	64·47	0·0914	9·071
0·2244	0·552	67·19	0·0462	8·994	0·1543	0·277	64·95	0·0240	9·082
			$(NO_2)(HSO_4)$.					$(NO_2)(HSO_4)$.	
0·3112	0·000	67·49	0·1008	8·543	0·1714	0·000	65·10	0·0597	8·853
0·1596	,,	,,	0·1759	8·033					
0·0787	,,	,,	0·2128	7·797					
0·1115	,,	,,	0·2654	7·328					

compositions are expressed as follows. The original oleum is regarded as a solution of disulphuric acid in sulphuric acid. Assuming the original presence of 1 mol. of disulphuric acid, solutions formed by the addition of quantities up to 0·5 mol. of nitric acid are treated as solutions of disulphuric acid, and of nitronium hydrogen disulphate formed from nitric acid and disulphuric acid by the completed reaction (5). According to this assumption, when exactly 0·5 mol. of nitric acid has been added, the disulphuric acid will have been destroyed, and the only solute component will be nitronium hydrogen disulphate. Any further quantities of nitric acid, up

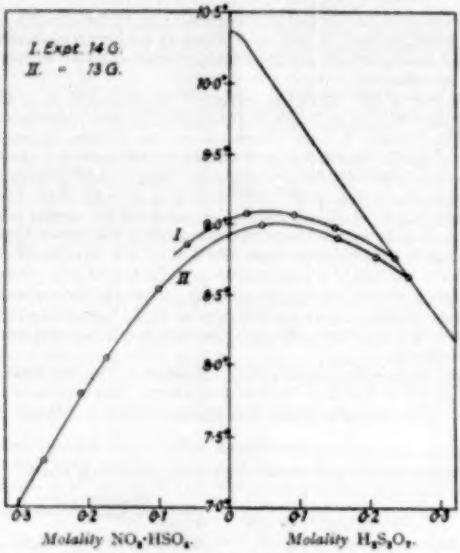
to a second 0·5 mol., are now assumed, for the purpose of expressing compositions, to react according to the following equation with the hydrogen disulphate ion which was formed from the first 0·5 mol.:

$$HNO_3 + HS_2O_7^- = NO_2^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This means that, during the addition of the second 0·5 mol. of nitric acid, composition is given in terms of the two solutes, nitronium hydrogen disulphate and nitronium hydrogen sulphate; and that when the second 0·5 mol. has been fully added, the solution contains only the one solute component, *viz.*, nitronium hydrogen sulphate. In the figure, the central vertical line (neutral line) represents compositions expressible in terms of nitronium hydrogen disulphate as the only solute. If we start with 1 mol. of disulphuric acid at some point on the nearly linear curve which slopes downward on the right-hand side of the diagram, then the addition

FIG. 1.

Freezing points of solutions of nitric acid in oleum solvents.



of 0·5 mol. of nitric acid, producing 0·5 mol. of nitronium hydrogen disulphate, carries us leftward to the neutral line, whilst the addition of another 0·5 mol. of nitric acid converts this nitronium hydrogen disulphate into 1 mol. of nitronium hydrogen sulphate, thereby taking us an equal distance to the left of the neutral line.

(3) *Qualitative Interpretation of the Freezing-point Curves.*—As will be seen from Fig. 1, the first effect of added nitric acid on the freezing point of oleum is to raise it. Now if the total solute in the original oleum were undissociated disulphuric acid, and if equation (5) were accurately to represent the stoicheiometry of the reactions undergone by nitric acid, then the freezing point would not be changed; for according to equation (5), two original solute molecules become replaced by two ions. The evident reason why the freezing point is raised by nitric acid is that the original disulphuric acid is considerably ionised according to equation (3), so that the loss of two stoicheiometric molecules of disulphuric acid involves the loss of more than two solute particles. There can be no doubt about the applicability of equation (5) in this region of composition; for disulphuric acid is still in large excess, and hence there can be no appreciable solvolysis of the hydrogen disulphate ion. When solvolysis does occur, each anion solvolysed produces one extra solute particle; and thus solvolysis tends to lower the freezing point.

As the addition of nitric acid is continued, but before the composition has been shifted quite as far as corresponds to the neutral line of Fig. 1, the freezing point approaches a somewhat flat maximum. The reason is that, in this region of composition, the large amount of hydrogen disulphate ion now present suppresses the ionisation of the small amount of disulphuric acid still remaining; this residue of substantially non-ionised disulphuric acid undergoes conversion, as we have seen, without change of freezing point.

The maximum is attained, and passed, a little before the neutral line, *i.e.*, a little before the solute composition is exactly that of nitronium hydrogen disulphate, because, when only a very small amount of free disulphuric acid remains, the solvolysis of the hydrogen disulphate ion begins to become appreciable; and the effect of that process, as has been noted, is to lower the freezing point.

At the neutral line, the composition of the solute can be expressed in terms of nitronium hydrogen disulphate as the only component; but owing to the solvolysis of this anion some nitronium hydrogen sulphate is present, and some free disulphuric acid still survives. The effect of added nitric acid on the freezing point is therefore a mixture of two effects, *viz.*, a decomposition of practically undissociated disulphuric acid, according to equation (5), without change in the number of solute particles, and a decomposition of the hydrogen disulphate ion, according to equation (7), with an increase in the number of solute particles. Therefore the freezing-point curve for added nitric acid in this region of composition slopes downward with only a moderate gradient.

As the addition of nitric acid is continued further, the last of the free disulphuric acid disappears, and the freezing-point curve falls more rapidly. The rough reason for this is that each added molecule of nitric acid is now producing two solute particles in accordance with equation (7). However, this is an inadequate description. Even when the free disulphuric acid has disappeared, the freezing point does not immediately begin to fall as rapidly as equation (7) would suggest. This is because, during the stage in which a good deal of hydrogen disulphate ion has not yet been desulphated by reaction (7), but a considerable concentration of hydrogen sulphate ion has nevertheless been built up, these two ions interact reversibly as follows:

$$HSO_4^- + HS_2O_7^- \rightleftharpoons H_2SO_4 + S_2O_7^{--} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

the basic hydrogen sulphate ion inducing a second stage of ionisation of the very weakly acidic hydrogen disulphate ion. The effect of this equilibrium is that, over the first region of composition that is traversed after the free disulphuric acid is destroyed, each added molecule of nitric acid will produce between one and two extra solute particles. The total reaction can be represented as a mixture of reaction (9), which produces one extra solute particle, and reaction (7) which produces two:

$$HNO_3 + 2HS_2O_7^- \rightleftharpoons NO_3^+ + S_2O_7^{--} + HSO_4^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In the next region of composition, when a large proportion of the hydrogen disulphate ion has been destroyed by processes (7) and (9), but most of the doubly charged disulphate ion has not yet been desulphated, the freezing-point curve will fall more rapidly than equation (7) would require. This is because desulphation of the normal disulphate ion sets in. Each molecule of added nitric acid then produces between two and three additional solute particles. The total reaction can be represented as a mixture of process (10), which gives three extra solute particles, and process (7) which produces two:

$$HNO_3 + S_2O_7^{--} + H_2SO_4 \rightleftharpoons NO_3^+ + 3HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Thus, as we pass towards the left from the neutral line in Fig. 1, by the progressive addition of nitric acid, the descending freezing-point curve steepens in a continuous manner.

When the amount of added nitric acid is sufficient to displace the solute composition just as far to the left of the neutral line as it started in the original oleum to the right of the neutral line, then disulphuric acid, in its molecular form and both its anionic forms, will have been fully destroyed (except for the very small amounts arising by self-dissociation of the sulphuric acid solvent). The solute composition will now be that of nitronium hydrogen sulphate; and furthermore, this salt will be substantially the only solute actually present in the dilute solution.

If still further amounts of nitric acid are added, the freezing-point curve continues to descend. We expect this, even though there can be no reaction between the solute nitronium hydrogen sulphate and the newly added nitric acid. We also expect the slope of the freezing-point curve to be somewhat steeper than before. For each added molecule of nitric acid will

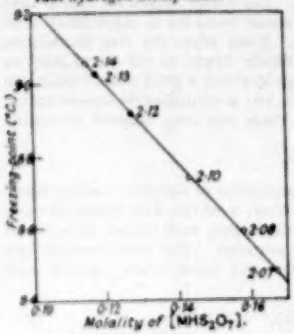
now ionise by reaction with the sulphuric acid solvent, and will therefore produce an average of nearly four extra solute particles, as is described in detail in Part III.

Part of the above description becomes quantitatively changed when we take into account the presence, ionisation, and desulphation of the higher polysulphuric acids (Part IV). In comparison with disulphuric acid, these higher acids are more easily ionised, and their ionisation tends more to proceed to a second stage; and they are also more easily desulphated than is disulphuric acid. Both the ionisations and the desulphations will be promoted by the basic materials which arise from the decompositions of the added nitric acid. These processes will have some effect, for instance, on the position of the freezing-point maximum, and on the position of the point at which the freezing-point curve cuts the neutral line. However, owing to the large tendency of the higher acids to desulphation, all these disturbances will diminish as one passes towards the left in Fig. 1. Furthermore, since the total destruction of the higher acids must precede that of disulphuric acid, the said disturbances must completely vanish well before that composition is reached at which even disulphuric acid, in all its forms, is practically completely absent, *i.e.*, the point at which the solute is nitronium hydrogen sulphate.

(4) *The v-Factors of Nitronium Hydrogen Disulphate.*—We proceed to check this interpretation quantitatively for certain specific compositions, first taking compositions represented by points on the neutral line, on which the total solute can be referred to the single component, nitronium hydrogen disulphate.

FIG. 2.

Comparison of the freezing points of solutions of nitronium and ammonium hydrogen disulphates.



(The figures in the diagram are the calculated v-factors—cf. Table II.)

If no solute were present except nitronium hydrogen disulphate, the v-factor at this composition would be 2. However, two disturbances combine to render the value not exactly equal to 2. First, some solvolysis of the hydrogen disulphate ion tends to raise the figure. Secondly, the formation of a certain quantity of doubly charged higher polysulphate ions tends to lower the figure. This second effect becomes more important in more concentrated solutions, and hence the v-factor, although it is greater than 2 in dilute solution, will fall as the concentration is increased.

The combined effect of these disturbances was analysed in some detail in Part IV, in connexion with the v-factors of ammonium hydrogen disulphate; and the solvolysis constant of the hydrogen disulphate ion, as well as an equilibrium constant connected with the formation of higher polysulphates, were extracted from the results. This case parallels the present example so closely that we may expect the freezing point of a solution of nitronium hydrogen disulphate to be practically the same as that of an equimolal solution of ammonium hydrogen disulphate; for the disturbances mentioned are both independent of the cation. Therefore one of the simplest tests that we can make of the preceding interpretation is to ascertain whether the freezing points of solutions of nitronium hydrogen disulphate, as given by the intersections of our freezing-point curves with the neutral line of Fig. 1, lie on a smooth curve drawn through the freezing points of solutions of ammonium hydrogen disulphate, as determined in Part IV. This test is shown in Fig. 2. The data required for it are given in columns 3 and 4 of Table II.

TABLE II.

*Freezing-point depressions and v-factors for nitronium hydrogen disulphate. Comparison with similar values for ammonium hydrogen disulphate.**

Expt.	Cation.	Molality.	F. p. (° c.).	$\Delta\theta'$.	$\Delta\theta''$.	ν'.	ν''.
106	NH_4^+	0·115	9·06	1·56°	1·48°	2·27	2·14
14 G	NO_2^+	0·117	9·03	1·59	1·51	2·23	2·13
13 G	NO_2^+	0·127	8·92	1·70	1·63	2·21	2·12
106	NH_4^+	0·143	8·74	1·88	1·81	2·19	2·10
105	NH_4^+	0·158	8·59	2·03	1·97	2·15	2·08
104	NH_4^+	0·167	8·48	2·14	2·08	2·14	2·07

* The values for the ammonium salts are taken from Table II of Part IV.

The last four columns in Table II are concerned with the calculation and comparison of ν-factors. Freezing-point depressions $\Delta\theta'$ are given, which are reckoned from the theoretical freezing point, 10·62°, of undissociated sulphuric acid. Some self-dissociation of the solvent contributes to these depressions. A correction for this effect having been applied, as described in Part IV, the corrected depressions $\Delta\theta''$ are listed.

The ν-factors which are calculated from the uncorrected depressions are given as ν′, whilst those which are computed from the corrected depressions are termed ν″. In these calculations it has been assumed that the solvation number of nitronium hydrogen disulphate is the same as that of nitronium hydrogen sulphate, *viz.*, 2 to the nearest unit, as given in Part III, just as the solvation number of ammonium hydrogen disulphate was taken in Part IV to be the same as that of ammonium hydrogen sulphate, *viz.*, 1, as found in Part I. It will be noted that the ν-factors of nitronium hydrogen disulphate interpolate themselves quite smoothly amongst the corresponding values of ammonium hydrogen disulphate.

The quantitative success of these tests shows that we were correct, not only in regarding equation (5) as a good approximate expression of the ionisation of nitric acid in oleum, but also in suggesting that more detailed specification of the process which involved assuming the first of equations (6) to be complete, and the second to lack completeness only on account of causes which have nothing to do necessarily with nitric acid, and only to extents which can be quantitatively estimated from independent studies of the equilibria involved.

(5) *The ν-Factor of Nitronium Hydrogen Sulphate.*—When 1 mol. of nitric acid has been added for each 1 mol. of disulphuric acid in the original oleum, the only solute present should be nitronium hydrogen sulphate. The ν-factor should therefore be 2·00. All such disturbances as are discussed in the preceding Section are absent.

From the graph of Expt. 13 G (cf. Fig. 1) it can be read that the freezing point of a 0·2545 molal solution of nitronium hydrogen sulphate in sulphuric acid is 7·42°. We have to consider to what extent the self-dissociation of the solvent is involved in this result. The ionic self-dehydration will not have been affected, and therefore the solvent freezing point from which the freezing-point depression due to the added solute should be computed is 10·52°, as was shown in Parts I and IV. The autoprotolysis of the solvent is not quite completely repressed, and 0·01° must be subtracted from the observed depression in order to allow for this. From the corrected depression, we may calculate the ν-factor of nitronium hydrogen sulphate, exactly as described for the ν-factor of ammonium hydrogen sulphate in Part IV, except that in the present case the solvation number 2 is used, in accordance with the decision reached in Part III concerning the solvation of the nitronium ion. The computed ν-factor for the nitronium salt is 1·99, in good agreement with expectation, again confirming the estimated freezing point, 10·52°, of the non-autoprotolysed solvent.

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502. *Cryoscopic Measurements in Sulphuric Acid. Part VI. The Solutes Nitronium Perchlorate and Ammonium Perchlorate. The Basicity of the Perchlorate Ion and the Acidity of Perchloric Acid. Notes on the Strengths of Some Oxy-acids.*

By R. J. Gillespie.

Nitronium perchlorate and ammonium perchlorate in solvent sulphuric acid produce freezing-point depressions which show that the anion of these salts is largely solvolysed to free perchloric acid. Perchloric acid is thus a very weak acid in sulphuric acid. Its acidity constant is deduced, as well as the solvolysis constant of the perchlorate ion.

Disulphuric acid was shown to be an acid of medium strength in sulphuric acid (Part IV). Thus disulphuric acid, perchloric acid, and sulphuric acid form a widely spaced acidity series, similar to acetic acid, phenol, and water, though on a displaced scale. It might have been expected, on the basis of known rules concerning the strengths of inorganic oxy-acids, that disulphuric acid would prove to be a much stronger acid than perchloric acid. It is suggested that the stabilisation of oxy-anions, relatively to the acids, by mesomeric charge-distribution among oxygen atoms having partial double bonds, is a prime factor determining the strengths of oxy-acids.

(1) *The ν-Factors of Nitronium and Ammonium Perchlorate.*—In an accompanying paper (*J.*, 1950, paper no. 503) Goddard, Hughes, and Ingold describe the preparation of a number of

crystalline nitronium salts. The first of these to be isolated in a pure state was nitronium perchlorate; and, when it was originally obtained, it was felt to be important to confirm that it had the expected ionic constitution. As regards the solid compound, the required evidence was provided by Dr. D. J. Millen by the method of Raman spectroscopy (*Nature*, 1946, **158**, 480; cf. *J.*, 1950, paper no. 509); and since then a complete *X*-ray analysis has been carried through by Professor E. G. Cox, Dr. G. A. Jeffery, and Mrs. M. R. Truter (*Nature*, 1948, **162**, 159). The author undertook to study the compound in solution in sulphuric acid, and in particular to ascertain whether, in such solutions, the solute is dissociated into its ions. The results were somewhat unexpected, and it therefore proved necessary to examine nitronium perchlorate and a well-known ionic perchlorate in parallel.

The first cryoscopic measurements on solutions of nitronium perchlorate in sulphuric acid revealed that this solute was producing approximately a three-fold, rather than a two-fold depression of the freezing point of the solvent. This suggested that, contrary to one's preconceptions, perchloric acid is so *weak* an acid that its salt was being nearly completely solvolysed.

In order to be certain that the observed effect was not a special property of the nitronium compound, but was really due to solvolysis of the perchlorate ion, some similar cryoscopic measurements were made with ammonium perchlorate as the solute. This salt also gave an approximately three-fold depression of the freezing point, in confirmation of the previous indication.

The incidental observation was made that dilute (say 0·05 molal) solutions of either nitronium perchlorate or ammonium perchlorate in sulphuric acid fume in ordinary air. This happens even when the solvent sulphuric acid has been pre-treated with a small amount (say 0·05 molal) of water, and so it cannot be due to an escape of sulphur trioxide from the solution. It is assumed to be due to the escape of perchloric acid, and thus to indicate the presence of the free acid in solution.

The freezing points of solutions of perchloric acid in sulphuric acid have been measured, though somewhat approximately, by Robles and Moles (*Anal. Fís. Quím.*, 1934, **32**, 474). They observed depressions corresponding to a normal molecular weight, and this is consistent with the conclusion that perchloric acid is ionised only to a very small extent in sulphuric acid.

On this evidence it is presumed that the reactions which take place on the dissolution of nitronium and ammonium perchlorates in sulphuric acid can be approximately represented as follows :

$$NClO_4 + H_2SO_4 = NO_2^+ + HClO_4 + HSO_4^-$$
$$NH_4ClO_4 + H_2SO_4 = NH_4^+ + HClO_4 + HSO_4^-$$

Accordingly, the ν-factors for each solute were calculated from the observed freezing-point depressions, using equation (5) of Part I, and substituting, in the first instance, $s_2 = 1$ and $\nu_2 = 3$ in the nearly-unit correction factor. This preliminary calculation made it obvious that the true ν-factors would prove to be a little less than 3.

The whole procedure was then refined by making allowance for the known disturbances. The first of these is ion solvation. It has been concluded already that nitronium and ammonium hydrogen sulphates have solvation numbers of approximately 2 and 1, respectively (cf. Parts I and III); and hence we should substitute $s_2 = 3$ in the case of nitronium perchlorate, and $s_2 = 2$ in that of ammonium perchlorate, instead of $s_2 = 1$, in the nearly-unit correction factor in equation (5) of Part I.

The second disturbance relates to the effect of the hydrogen sulphate ion, which is produced by the solvolysis of the perchlorates, first in repressing the ionisation of the pre-treatment water, and secondly in repressing the residual autoprotolysis of the solvent sulphuric acid. These effects make the apparent freezing-point depressions ($\Delta\theta$), given by the added perchlorate, too small. A correction for this was calculated by a method of cyclic approximation. Initially the solvolysis of the perchlorate ion was taken to be complete, and, using the autoprotolysis constant of sulphuric acid, and the data given in Part II for the degree of ionisation of water, an approximate correction to the observed freezing-point depression was calculated. From this, an approximate ν-factor was computed, which was then used in order to calculate a better approximation to the quantity of hydrogen sulphate ion which is formed by solvolysis of the perchlorate ion, and hence to calculate a better approximation to the correction to be applied to the observed freezing-point depressions. From the corrected depression ($\Delta\theta'$), an improved ν-factor was calculated using the appropriate form of equation (5) of Part I. The results of the measurements, and the final values of the ν-factors calculated from them, are in Table I.

TABLE I.

Freezing points of solutions of perchlorates in sulphuric acid.

Molality of salt (Δm_2).	F. p. (° c.).	Depressions. Obs. $\Delta\theta$.	Corr. $\Delta\theta$.	ν-Factor.	Molality of salt (Δm_2).	F. p. (° c.).	Depressions. Obs. $\Delta\theta$.	Corr. $\Delta\theta$.	ν-Factor.
Expt. No. 31. Salt = NH_4ClO_4. Molality of water (m_1) = 0·075.					Expt. No. 17. Salt = NO_2ClO_4. Molality of water (m_1) = 0·060.				
—	9·720	—	—	—	—	9·886	—	—	—
0·00696	9·598	0·122°	0·124°	2·96	0·00654	9·774	0·112°	0·115°	2·91
0·03055	9·189	0·531	0·544	2·95	0·01508	9·625	0·261	0·286	2·92
0·04526	8·939	0·781	0·800	2·93	0·02734	9·405	0·481	0·489	2·95
0·06405	8·611	1·109	1·133	2·93	0·03637	9·240	0·646	0·656	2·97
0·07907	8·349	1·371	1·397	2·93				Mean	2·94
0·08800	8·218	1·502	1·529	2·88					
			Mean	2·93					

(2) *The Solvolysis (or Basicity) Constant of the Perchlorate Ion.*—The result that the ν-factors for nitronium and ammonium perchlorate are not exactly equal to 3 means that the chemical equations written above do not accurately represent the stoicheiometry of the processes which take place when the salts are dissolved in the solvent. It means, in short, that the solvolytic process

$$ClO_4^- + H_2SO_4 \rightleftharpoons HClO_4 + HSO_4^-$$

is appreciably incomplete.

We can employ the determined ν-factors in order to compute the equilibrium constant for this solvolytic reaction—in other words, the constant which represents the basic strength of the perchlorate ion. The derived values are highly sensitive to experimental error, because they depend essentially on the small differences between ν and 3; but the calcuation has been made, using the data for ammonium perchlorate, which are slightly better than those obtained for the nitronium salt. The results are given in Table II.

The solvolysis constant being defined by the equation

$$K_b(ClO_4^-) = [HClO_4][HSO_4^-]/[ClO_4^-]$$

with the concentration expressed in molalities, K_b has been computed from the cryoscopic results by means of the equation

$$K_b = \{(\nu - 2)^2\Delta m_2 + (\nu - 2)m_1\}/(3 - \nu)$$

where Δm_2 is the molality of the salt, and m_1 is that of the hydrogen sulphate ion produced from the water with which the solvent was pre-treated. The concentration m_1 was computed from the data given in Part II for the degree of ionisation of water in sulphuric acid, due allowance being made for the effect of the presence of extraneous hydrogen sulphate ions, which in this case was that produced by solvolysis of the perchlorate ion; and the concentration of this hydrogen sulphate ion was calculated, with sufficient accuracy to provide a starting point for the calculation of m_1, simply from the concentration of added perchlorate and the observed ν-factor.

TABLE II.

Solvolysis of ammonium perchlorate in sulphuric acid (Expt. 31).

Δm_2.	m_1.	ν.	$K_b(ClO_4^-)$.	Δm_2.	m_1.	ν.	$K_b(ClO_4^-)$.
0·00696	0·0720	2·96	1·88	0·06405	0·0689	2·93	1·70
0·03055	0·0703	2·95	2·08	0·07907	0·0687	2·93	1·87
0·04526	0·0697	2·93	1·62	0·08800	0·0682	2·88	1·04
						Mean	1·70

Adopting the value $K_b(ClO_4^-) = 1·7$ g.-mol. kg.$^{-1}$, and reversing the process of calculation, theoretical curves have been constructed for the depression of the freezing point of sulphuric acid by ammonium perchlorate. Such a curve, drawn for the case in which the solvent has been pre-treated with water in 0·075 molal concentration, is shown in Fig. 1, in association with the experimental points for nitronium and ammonium perchlorates.

(3) *The Acidity Constant of Perchloric Acid.*—From the value $K_b(ClO_4^-) = 1·7$ g.-mol. kg.$^{-1}$ for the solvolysis constant of the perchlorate ion, and the figure deduced in Part IV (*J.*, 1950, 2516) for the autoprotolysis constant of sulphuric acid, $K_{ap} = [H_3SO_4^+][HSO_4^-] =$

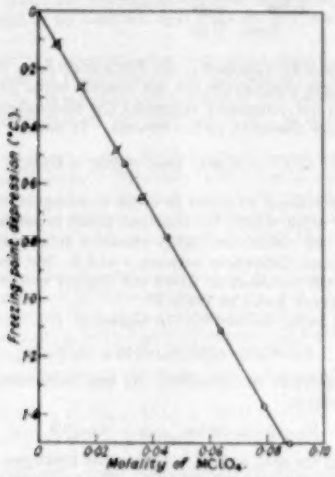
$1{\cdot}7 \times 10^{-4}$ g.-mol.$^{\frac{1}{2}}$ kg.$^{-\frac{1}{2}}$, one can calculate the acid dissociation constant of perchloric acid in sulphuric acid. We have

$$K_a(HClO_4) = \frac{[H_2SO_4^+][ClO_4^-]}{[HClO_4]} = \frac{K_m(H_2SO_4)}{K_b(ClO_4^-)} = 1{\cdot}0 \times 10^{-4} \text{ g.-mol. kg.}^{-1}$$

(4) *Note on the Acidities of Oxy-acids.*—In Parts II and IV (*J.*, 1950, 2493, 2516) the first dissociation constant of disulphuric acid was found to be $K_a(H_2S_2O_7) = 0{\cdot}020$ g.-mol. kg.$^{-1}$. The value now obtained for the dissociation constant of perchloric acid is $K_a(HClO_4) = 0{\cdot}00010$ g.-mol. kg.$^{-1}$. Thus, in sulphuric acid as solvent, disulphuric acid is a much stronger acid than is perchloric acid.

FIG. 1.

Theoretical curve ($K_b = 1{\cdot}7$) *for the depression of the freezing point of sulphuric acid by ionising perchlorates.*



Experimental points for nitronium perchlorate -○-.
" " *ammonium perchlorate* ○.

Now although perchloric acid has long been regarded as the strongest known acid, it could have been deduced, from certain proposed relationships between the aqueous ionisation constants of inorganic oxy-acids, that disulphuric acid would be stronger. Kossiakoff and Harker (*J. Amer. Chem. Soc.*, 1938, **60**, 2047) calculated the aqueous ionisation constants of a number of inorganic oxy-acids on the basis of the assumption that all the acids possess single-bonded octet structures, and that differences of acidity can be attributed to differences of the electrostatic energy of removal of the proton from the acid to the surrounding water. This method has been criticised by Ricci (*ibid.*, 1948, **70**, 109), who has shown that the aqueous pK values of oxy-acids H_aXO_b, of any total charge, are given to the same order of accuracy, *viz.*, to about one pK unit, by the purely empirical equation, $pK = 8 - 9m + 4n$, where m is the formal positive charge on the central atom, X, and $n = b - a$ is the number of formal negative charges carried by the oxygen atoms, and the word " formal " means computed for the equal sharing of electron-duplets in single-bonded octet structures. He has applied this formula with similar success to complex acids, such as diphosphoric acid, $H_4P_2O_7$, by treating the central group, POP in this case, as a " compound atom " X in the formula H_aXO_b. Pauling (" General Chemistry," Freeman, San Francisco, 1947, p. 394) has also given rules for the evaluation of approximate aqueous ionisation constants of inorganic oxy-acids $XO_n(OH)_a$: the first rule states that successive ionisation constants, K_1, K_2, K_3 . . . stand in the ratio $1 : 10^{-5} : 10^{-10}$ . . . , and the second rule is that first ionisation constants are given approximately by the formula $pK_1 \sim 7 - 5n$.

Assuming that these rules and methods have a certain validity for very strong acids (for

which they cannot directly be tested), we may compute theoretical aqueous pK values for acids such as sulphuric and perchloric acids; and we may even include disulphuric acid in the treatment by adopting Ricci's device of regarding the central group, here SOS, as the compound atom X. The results of these calculations are in Table III.

TABLE III.

*Calculated aqueous p*K *values of some strong acids.*

Method.	H_2SO_4: pK_1.	$HClO_4$: pK.	$H_2S_2O_7$: pK_1.	pK_2.
Kossiakoff and Harker	−3·0	−7·3	—	—
Ricci	−2	−7	−12	−8
Pauling	−3	−8	−13	−8

Thus it appears that, so far as first ionisations are concerned, disulphuric acid, perchloric acid, and sulphuric acid form a widely-spaced series in order of decreasing acidity, comparable, though on a displaced scale, to the series acetic acid (pK 5), phenol, (pK 10), and water (pK 16). Perhaps, therefore, one should have expected that disulphuric acid would be a somewhat weak acid, and perchloric acid a very weak acid, in solvent sulphuric acid, just as acetic acid is a somewhat weak acid, and phenol a very weak acid, in solvent water. It does not seem to have been established (or even, as far as is known, suggested) before that disulphuric acid is in principle a much stronger acid than perchloric acid.

The structural basis of the methods of calculation mentioned above has previously received a certain amount of discussion. The electrostatic calculations of Kossiakoff and Harker were based on single-bonded octet structures. The parameters in Ricci's equation were related to the formal charges of octet structures, though it would be possible to give other structural meanings to the same quantities. Pauling stated that his second rule can be understood on the basis that the charge on the anion of the acid becomes more divided, and therefore less potent in attracting the hydrogen ion, the larger the value of n. However, this idea seems hardly consistent with his view (*op. cit.*, p. 163) that the most important of the structures of the oxy-acids are the octet structures, in which every single-bonded, non-hydroxyl, oxygen atom carries a formal negative charge.

Hunter, Phillips, and Sutton (*J.*, 1945, 146) have presented a strong case in favour of the view that, in compounds such as oxy-acids, the oxygen atoms, which in octet formulæ would be singly-bonded and have formal negative charges, are more correctly represented as doubly-bonded and without formal charges, as in classical chemical formulæ. It is possible with the aid of such doubly-bonded structures to understand how the oxy-acids fall into distinct groups with respect to their dissociation constants, as is illustrated in Table IV; for the larger the number of double bonds, the more the total charge can become distributed in the mesomeric anion, thus increasing its relative stability. In the Table, the recorded pK values are taken

TABLE IV.

Classification of aqueous ionisation constants of inorganic oxy-acids.

Group 1.

$X(OH)_n$ (very weak acids).

	pK_1 (1).	pK_2 (1).
$B(OH)_3$	9·2	—
$Si(OH)_4$	10·0	—
$Ge(OH)_4$	8·6	12·7
$As(OH)_3$	9·2	—
$Sb(OH)_3$	11·0	—
$Te(OH)_6$	6·2, 8·8	10·4
$Cl(OH)$	7·2	
$Br(OH)$	8·7	
$I(OH)$	11·0	

Group 2.

$XO(OH)_n$ (weak acids).

	pK_1 (1/2).	pK_2 (2/3).
$PO(OH)_3$	2·1	7·2
$HPO(OH)_2$	1·8	6·2
$H_2PO(OH)$	2·0	
$AsO(OH)_3$	2·3	7·0
$NO(OH)$	3·3	
$SO(HO)_2$	1·9	7·0
$SeO(OH)_2$	2·6	8·3
$TeO(OH)_4$	2·7	8·0
$ClO(OH)$	2·0	
$IO(OH)_3$	1·6	6·0

Group 3.

$XO_2(OH)_n$ (strong acids).

	pK_1 (1/3).	pK_2 (1/2).
$SO_2(OH)_2$	—	1·9
$SeO_2(OH)_2$	—	2·0
$IO_2(OH)$	0·8	

Group 4.

$XO_3(OH)_n$ (very strong acids).

	pK_1 (1/4).
$ClO_3(OH)$	—
$MnO_3(OH)$	—

from lists given by Ricci and Pauling, and, as an indication of the degree of distribution of the anionic charge, a figure is given, against each heading " pK," which is the value in electronic units of the charge carried by one oxygen atom.

Obviously factors other than charge distribution among atoms enter into the determination of pK values. The effect of the electronegativity of the central atom is clearly seen in a series such as Cl(OH), Br(OH), I(OH), or $SO(OH)_2$, $SeO(OH)_2$, $TeO(OH)_2$. It is to induced electronegativity, *i.e.*, to the inductive effect of an acyl group introduced in place of hydrogen, that one attributes the greater strengths of poly-acids than of their parents, as is illustrated by the comparison of diphosphoric acid, $pK_1 = 0{\cdot}9$, with phosphoric acid, $pK_1 = 2{\cdot}1$, or of disulphuric acid with sulphuric acid as discussed above.

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503. *Cryoscopic Measurements in Sulphuric Acid. Part VII. The Basicity of Nitro-compounds, Sulphonyl Compounds, and Sulphuryl Compounds in Sulphuric Acid.*

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It is shown, by measurement of the freezing points of solutions in sulphuric acid, that nitro-compounds ionise as bases in that solvent. The basicity constants are determined for nitromethane, nitrobenzene, the *p*-methyl and *m*-ammonium substitution products of nitrobenzene, and for 2 : 4 : 6-trinitrotoluene. The proportions in which these compounds are ionised in 0·1 molal solution in anhydrous sulphuric acid at its freezing point range from about 29% (*e.g.*, trinitrotoluene) to about 70% (*p*-nitrotoluene).

By the same method, it is shown that benzenesulphonic acid and *p*-toluenesulphonic acid, as well as diphenyl sulphone, are likewise considerably ionised as bases in sulphuric acid. The basicity constants of these solutes are determined. A similar study of the solute ethyl alcohol indicates that it is converted substantially quantitatively into ethylsulphuric acid (ethyl hydrogen sulphate), which is also appreciably ionised.

Constitutional effects on basicity are considered. Reference is made to the bearing of this form of ionisation on the kinetics of aromatic nitration in sulphuric acid, *e.g.*, of nitro-compounds.

(1) *Basicity and Nitration Rate in Sulphuric Acid.*

IT was recently pointed out (Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277) that rates of nitration in a strongly acidic medium such as sulphuric acid cannot but be dependent on the condition of the aromatic compound in such solutions. The great majority of those organic compounds that are soluble in sulphuric acid behave as bases in that solvent, taking up a proton with conversion into a cation. In this ionisation, an intermediate hydrogen-bond complex is often produced in considerable proportion—just as when ammonia functions as a base in water (Moore and Winmill) :

$$B + H_2SO_4 \rightleftharpoons BHSO_4H \rightleftharpoons BH^+ + SO_4H^-$$

Having summarised the evidence, largely based on cryoscopic and solubility data, in favour of this picture of sulphuric acid solutions, Gillespie and Millen noted that, since the complex $BHSO_4H$, and still more, the cation BH^+, will certainly have a depressed nuclear reactivity towards electrophilic reagents, nitration rate would be expected often to depend on the surviving proportion of free base B, and on the degree of incompletness of conversion into the cation BH^+. They pointed out, further, that this effect could constitute one contributory cause of the well-established result that rates of nitration in sulphuric acid are first increased, and then decreased, by the progressive addition of water. Although water is a moderately strong base in sulphuric acid, it is known that the first 30 mols. per cent. of water do not destroy much nitronium ion; and hence one of their main kinetic effects on a nitration might be to cause the replacement of a less reactive by a more reactive form of the aromatic compound. Illustrations will be given later which show that very small proportions of water can cause substantial replacements of this type. Larger amounts of water will have a solvent effect (Gillespie, Hughes, Ingold, Millen, and Reed, *Nature*, 1949, **163**, 599; Hughes, Ingold, and Reed, *J.*, 1950, 2400). Large proportions of water will destroy the nitronium ion.

A quantitative interpretation of the recorded results on the kinetics of nitration in sulphuric acid (Martinsen, *Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605; Klemenc and Schöller, *Z. anorg. Chem.*, 1924, **141**, 231; Lauer and Oda, *J. pr. Chem.*, 1936, **144**, 176; Oda and Ueda,

Bull. Inst. Phys. Chem. Res. Japan, 1941, **20**, 335; Lantz, *Bull. Soc. chim.*, 1939, **6**, 280 *et seq.*; Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871; Bennett, Brand, James, Saunders, and Williams, *J.*, 1947, 474) would require more knowledge than we yet possess concerning the proportions in which undissociated salts and cations are formed from aromatic compounds. The acceleration of nitration by limited additions of water to the solvent sulphuric acid have been reported for nitro-compounds, sulphonic acids, anthraquinones, and benzoic acids. It is already established that ketones, including anthraquinone, and carboxylic acids, including benzoic acid, function as strong bases in sulphuric acid, undergoing practically complete conversion into cationic forms in the anhydrous acid. For one ketone, acetone, and one carboxylic acid, acetic acid, the substantial completeness of the ionisation was illustrated in Part I (*J.*, 1950, 2473). The experiments on anthraquinone and benzoic acid will be published later. It will be shown in this paper that nitro-compounds and sulphonic acids also behave as bases in sulphuric acid, but weaker ones, undergoing considerable, though only partial, conversion into cationic forms.

(2) *Basicity of Nitro-compounds in Sulphuric Acid.*

(2.1) *Previous Investigations.*—Hantzsch was the first to show, by cryoscopic and conductometric methods, that many organic substances behave as bases when dissolved in sulphuric acid (*Z. physikal. Chem.*, 1907, **61**, 257; **62**, 626; 1908, **65**, 41. Cf. Oddo and Scandola, *Gazzetta*, 1908, **38**, 603; 1909, **39**, I, 569; 1909, **39**, II, 1; 1910, **40**, II, 163; Oddo and Casalino, *ibid.*, 1917, **47**, II, 200, 2321. Cf. also Hantzsch, *Ber.*, 1925, **58**, 941). He concluded, albeit on the basis of a somewhat qualitative investigation, that certain of the solutes he examined, *e.g.*, ethyl ether, acetophenone, benzoic acid, *p*-nitroaniline, and 2 : 4-dinitroaniline, underwent complete ionisation in the solvent :

$$B + H_2SO_4 = BH^+ + HSO_4^-$$

Other solutes, such as dichloroacetic acid and *p*-nitrotoluene, appeared to be partly ionised. Yet others, notably trichloroacetic acid, nitromethane, *m*-dinitrobenzene, 2 : 4-dinitromesitylene, 1 : 3 : 5-trinitrobenzene, 2 : 4 : 6-trinitrotoluene, and picric acid, were concluded to dissolve without any form of change. The last four of these compounds were employed by Hantzsch for his determination of the cryoscopic constant of sulphuric acid.

The conclusion that aromatic polynitro-compounds (except nitroanilines) dissolve as non-electrolytes in sulphuric acid has been accepted by all who have since studied the properties of that solvent : Oddo and Scandola (*Gazzetta*, 1918, **48**, II, 17), Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900), and Robles and Moles (*Anal. Fís. Quím.*, 1934, **32**, 474) all employed 1 : 3 : 5-trinitrobenzene and picric acid in their experimental determinations of the cryoscopic constant of sulphuric acid.

Hantzsch's conclusion that *p*-nitrotoluene is partly ionised in sulphuric acid was indirectly confirmed by Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1708), who, in a more accurate study of the cryoscopic behaviour of nitrobenzene in sulphuric acid, found that nitrobenzene was partly ionised, having a ν-factor of about 1·2.

In the course of their search for compounds which behave as simple bases in sulphuric acid, Hammett and Deyrup (*loc. cit.*) investigated the depressions of freezing point given by a number of nitroanilines. *o*-Nitroaniline, *p*-chloro-*o*-nitroaniline, 2 : 4-dichloro-6-nitroaniline, 2 : 4-dinitroaniline, 2 : 6-dinitro-4-methylaniline, 6-bromo-2 : 4-dinitroaniline, 2 : 4 : 6-trinitroaniline, and 2 : 4 : 6-trinitro-*NN*-dimethylaniline, all gave ν-values of approximately 2·0. It was concluded that they all behaved as simple bases, ionising completely according to the general equation given above.

(2.2) *The Solute* 2 : 4 : 6-*Trinitrotoluene.*—For the present work, this substance was chosen as the representative polynitro-compound. The observed freezing points of its solutions in sulphuric acid, containing a small amount of added water, are recorded in Table I. For the calculation of ν-factors it is a sufficient approximation to employ equation (5) of Part I (*J.*, 1950, 2473) with the substitution $s_3 = 1$ and $\nu_3 = 1$ in the nearly-unit correction factor. A value of unity is taken for s_3, because it is very likely that the non-ionised form of this and other nitro-compounds in sulphuric acid is not the free molecule but is a definite hydrogen-bonded compound with a molecule of sulphuric acid (cf. p. 2542, and Gillespie and Millen, *loc. cit.*). The values of the ν-factor thus derived are given in Table I. They indicate approximately 9% of ionic dissociation in the range of concentration studied. From the figures one may compute the equilibrium constant

$$K_3(C_6H_2Me(NO_2)_3) = [C_6H_2Me(NO_2)_3H^+][HSO_4^-]/[C_6H_2Me(NO_2)_3]$$

representing the basic strength of 2 : 4 : 6-trinitrotoluene in sulphuric acid. The concentrations being expressed in molalities, this constant may be computed by means of the formula

$$K_b = [(\nu - 1)^2\Delta m_2 + (\nu - 1)m_a]/(2 - \nu)$$

where Δm_2 is the molality of the nitro-compounds and m_a that of the hydrogen sulphate ion formed from the water present. This latter quantity is easily calculated, as has already been outlined in Part I, from the concentration of water m_0 and its known ν-factor. The values of K_b are shown in Table I.

TABLE I.

Freezing points of solutions of 2 : 4 : 6-*trinitrotoluene in sulphuric acid* (Expt. 39).

Molality of water (m_0).	Molality of $C_6H_2Me(NO_2)_3$ (Δm_2).	F. p. (° c.).	ν-Factor.	K_b (g.-mol. kg.$^{-1}$).
0·074	—	9·691	—	—
,,	0·0222	9·544	1·09	0·0068
,,	0·0385	9·437	1·09	0·0069
,,	0·0537	9·337	1·09	0·0071
,,	0·0721	9·215	1·09	0·0072
,,	0·0963	9·064	1·07	0·0057
			Mean	0·0067

2 : 4 : 6-Trinitrotoluene is thus a somewhat weak base with $K_b = 0{\cdot}0067$ g.-mol. kg.$^{-1}$ in sulphuric acid. Although the other polynitro-compounds, which have formerly been claimed to dissolve in sulphuric acid without ionisation, have not been re-examined, it cannot be doubted that they are all bases of appreciable strength. On theoretical grounds one might expect the least basic of them to be 1 : 3 : 5-trinitrobenzene and picric acid; and it happens that these compounds were studied by Hammett and Deyrup (*loc. cit.*). Their freezing-point depressions, together with our value of the cryoscopic constant of sulphuric acid, indicate several units per cent. of ionisation in the solutions investigated. The data of Hammett and Deyrup are not accurate enough to permit the calculation of basicity constants, but such constants could be determined by the cryoscopic method. Clearly, polynitro-compounds should not be used to determine the cryoscopic constant of sulphuric acid.

(2.3) *The Solute* m-*Nitroaniline.*—Since two nitro-groups, both *m*-situated with respect to a given nitro-group, do not attract electrons from the latter sufficiently strongly to suppress completely its measurably basic behaviour in sulphuric acid, it was to be expected that a single *m*-situated ammonium pole would also be unable fully to suppress similarly manifested basic character in the nitro-group. The point has been tested by means of the cryoscopic study, recorded in Table II, of *m*-nitroaniline in solvent sulphuric acid. The observed freezing-point depressions are given under the heading ($\Delta\theta_1$). They have to be corrected, in the manner outlined in Part I, for the repression of the ionisation of the water present, and for repression of the autoprotolysis of the solvent, by the hydrogen sulphate ion which is formed in the first ionisation of the *m*-nitroaniline. The corrected freezing-point depressions are given in the table under the heading ($\Delta\theta_2$). From these corrected depressions ν-factors have been calculated by means of the usual equation (Part I) after substitution of $s_2 = 2$ and $\nu_2 = 2$. This substitution assumes that the *m*-nitroanilinium ion, like other nitro-compounds, forms a hydrogen-bonded compound with one molecule of sulphuric acid. The resulting ν-factors show that *m*-nitroaniline is acting to an appreciable extent as a di-acid base. Values of its second-stage ionisation constant, defined by

$$K_2[\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}NO_2] = [\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}\overset{+}{N}O_2H][HSO_4^-]/[\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}NO_2]$$

with the concentrations in molalities, and therefore calculated by means of the formula

$$K_2^* = [(\nu - 1)(\nu - 2)\Delta m_2 + (\nu - 2)m_a]/(3 - \nu)$$

are given in the table. The basic strength of the cation *m*-$\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}NO_2$, evidently exerted through its nitro-group, is represented by the basicity constant 0·014 g.-mol. kg.$^{-1}$.

No *o*- or *p*-nitro-substituted anilines have been investigated in the present work; but Hammett and Deyrup concluded (*loc. cit.*) that *o*-nitroaniline and 2 : 4-dinitroaniline, as well as several of their substitution products, behave as mono-acid bases in sulphuric acid. This interpretation would mean that they are completely converted into anilinium ions, and then, having acquired an ammonium pole, become quite incapable of a second stage of ionisation

involving proton-uptake by an *o*- or *p*-situated nitro-group. Whether or not the separation of the stages of ionisation is quite as sharp as this, we should, on theoretical grounds, expect it to be substantially sharper for these *o*- and *p*-nitro-compounds than for the *m*-nitro-compound. A comparison of Hammett and Deyrup's results for the *o*- and *p*-nitro-compounds with the present results for *m*-nitroaniline suggests that in fact the *o*- and *p*-nitro-substituted anilinium ions are less basic than is the *m*-nitroanilinium ion, though the data for the *o*- and *p*-compounds are not quite precise enough to permit a quantitative assessment of the differences.

TABLE II.

Freezing points of solutions of m-*nitroaniline in sulphuric acid* (Expt. 91).

Molality of			Depressions			
water (m_0).	m-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ (Δm_2).	F. p. (° c.).	$\Delta\theta_1$.	$\Delta\theta_2$.	ν-Factor.	K_b (g.-mol. kg.$^{-1}$).
0·052	—	9·959	—	—	—	—
,,	0·01045	9·834	0·125°	0·131°	2·08	0·010
,,	0·02536	9·654	0·305	0·317	2·11	0·016
,,	0·03191	9·569	0·390	0·405	2·10	0·015
,,	0·03712	9·504	0·455	0·473	2·10	0·016
					Mean	0·014

The reciprocal effect of nitro-groups on an amino-group can be observed: three *o*- and *p*-situated nitro-groups appreciably impede even the first stage of ionisation of an aniline in sulphuric acid. 2 : 4 : 6-Trinitroaniline provides the illustration: for the data which Hammett and Deyrup record (*loc. cit.*) prove that this base is by no means fully converted into the anilinium ion when dissolved in sulphuric acid. This can be shown in two ways.

First, the ν-factor given by Hammett and Deyrup for 2 : 4 : 6-trinitroaniline, *viz.*, 1·83, is notably lower than those which they obtained for *o*-nitroaniline, 2 : 4-dinitroaniline, and the other nitro-anilines, which were concluded to dissolve as binary electrolytes. It is true that the ν-factors recorded by these authors are only approximate; but when allowance is made for this, it would appear that the real ν-factor for 2 : 4 : 6-trinitroaniline cannot lie higher than about 1·90. That is, the sulphuric acid solutions must contain an amount of the order of 10% of the free base.

A second method of estimating the incompleteness of the ionisation can be based on the use of Hammett's acidity function H_0. Its value for anhydrous sulphuric acid is $-10{\cdot}60$. The extent to which a base B is converted into its conjugate acid BH^+ depends only on the strength of the base and the acidity function of the solvent, the relation being

$$H_0 = pK_a + \log([B]/[BH^+])$$

where the strength of the base is represented by the acidity constant K_a of the conjugate acid:

$$pK_a = -\log\{(H^+)(B)/(BH^+)\}$$

(the parentheses denote activities). The basic strength of 2 : 4 : 6-trinitroaniline, as determined by the indicator method (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827), is given by the value $pK_a = -9{\cdot}29$. From these figures it can be computed that in fully anhydrous sulphuric acid 2 : 4 : 6-trinitroaniline should remain non-ionised to the extent of 5%. For the very slightly aqueous sulphuric acid employed in cryoscopic measurements on bases, the proportion of non-ionised amine would be greater. For instance, in a solution 0·05 molal with respect to water, and 0·05 molal with respect to 2 : 4 : 6-trinitroaniline the proportion of the latter remaining un-ionised would be 10%. The two estimates of the incompleteness of the ionisation are thus in satisfactory agreement.

(2.4) *The Solute Nitrobenzene.*—As is noted above, the cryoscopic work of Hantzsch, and especially of Hammett, leaves no doubt of the fact that nitrobenzene behaves as a base in sulphuric acid. Some new cryoscopic measurements, which are recorded in Table III, were carried out with the object of determining, for this parent aromatic nitro-compound, the basic strength as defined by the equilibrium constant

$$K_b(C_6H_5{\cdot}NO_2) = [C_6H_5{\cdot}NO_2H^+][HSO_4^-]/[C_6H_5{\cdot}NO_2]$$

the concentrations being as usual in molalities. The observed depressions ($\Delta\theta_1$) have to be corrected for the repression of the ionisation of water, and of the autoprotolysis of sulphuric acid, by the hydrogen sulphate ion formed by the ionisation of the nitrobenzene. These corrected depressions ($\Delta\theta_2$) were used in order to calculate the ν-factors by means of the usual

equation with the substitution $s_2 = 1$ and $\nu_2 = 1{\cdot}3$ in the correction factor. The basicity constant K_b was calculated by using the equation

$$K_b(C_6H_5{\cdot}NO_2) = \{(\nu - 1)^2\Delta m_2 + (\nu - 1)m_2\}/(2 - \nu)$$

and the values obtained are in the table. It appears that 27% of nitrobenzene is ionised in a 0·1 molal solution in the slightly aqueous sulphuric acid used. From the basicity constant $K_b = 0{\cdot}29$ g.-mol. kg.$^{-1}$ it can be computed that about 41% of the nitrobenzene would be ionised in a 0·1 molal solution in anhydrous sulphuric acid.

TABLE III.

Freezing points of solutions of nitrobenzene in sulphuric acid (Expt. 41).

Molality of water (m_1).	Molality of $C_6H_5{\cdot}NO_2$ (Δm_2).	F. p. (° c.).	Depression. $\Delta\theta_1$.	Depression. $\Delta\theta_2$.	ν-Factor.	K_b (g.-mol. kg.$^{-1}$).
0·039	—	9·871	—	—	—	—
,,	0·0426	9·558	0·313°	0·318°	1·23	0·019
,,	0·0844	9·230	0·641	0·651	1·27	0·028
,,	0·1121	9·031	0·840	0·853	1·28	0·033
,,	0·1383	8·823	1·048	1·063	1·27	0·033
,,	0·1585	8·688	1·183	1·200	1·25	0·031
					Mean	0·029

Hammett and Chapman have noted (*J. Amer. Chem. Soc.*, 1934, **56**, 1282) that the solubility of nitrobenzene in aqueous sulphuric acid becomes suddenly great at sulphuric acid concentrations at which the acidity of the medium is still much too small to allow any significant amount of conversion of the nitrobenzene into its conjugate acid. They point out that, in order to account for the solubility increase, some form of interaction between nitrobenzene and sulphuric acid must be assumed, other than an ionising proton-transfer.

A compound, $C_6H_5{\cdot}NO_2{,}H_2SO_4$, having considerable stability, has been described by Cherbuliez (*Helv. Chim. Acta*, 1923, **6**, 281) and by Masson (*J.*, 1931, 3200). Its melting point, 11·6°, is higher than that of either of its components. Masson regarded it as an ionised salt. However, the cryoscopic data show that, in solution in excess of sulphuric acid, most of it remains un-ionised, except at *very* low concentrations. On these grounds, Gillespie and Millen (*loc. cit.*) have assumed it to be the hydrogen-bonded precursor of the ionised salt, and to be the compound whose formation is responsible for the solubility effects studied by Hammett and Chapman.

(2.5) *The Solute* p-*Nitrotoluene.*—The introduction of a methyl group in the *para*-position to the nitro-group in nitrobenzene would be expected appreciably to enhance the basicity of this nitro-group. *p*-Nitrotoluene had been investigated by Hantzsch, who concluded that it was partly ionised. Some new cryoscopic measurements, which are recorded in Table IV, have now been carried out in order to determine the value of its basicity constant, defined by the equation

$$K_b(CH_3{\cdot}C_6H_4{\cdot}NO_2) = [CH_3{\cdot}C_6H_4{\cdot}NO_2H^+][HSO_4^-]/[CH_3{\cdot}C_6H_4{\cdot}NO_2]$$

concentrations being as usual in molalities. Calculations of the ν-factors, and of K_b, were made exactly as for nitrobenzene, and the results are in Table IV. In the nearly-unit correction factor of the usual freezing-point equation, the substitutions $s_2 = 1$ and $\nu_2 = 1{\cdot}6$ were made. It appears that about 60% of the *p*-nitrotoluene is ionised in a 0·1 molal solution in the slightly aqueous sulphuric acid used. From the basicity constant, $K_b = 0{\cdot}20$ g.-mol. kg.$^{-1}$, it can be calculated that about 73% of the *p*-nitrotoluene is ionised in a 0·1 molal solution in anhydrous sulphuric acid.

TABLE IV.

Freezing points of solutions of p-*nitrotoluene in sulphuric acid* (Expt. 108).

Molality of water (m_1).	Molality of p-$CH_3{\cdot}C_6H_4{\cdot}NO_2$ (Δm_2).	F. p. (° c.).	Depressions. $\Delta\theta_1$.	Depressions. $\Delta\theta_2$.	ν-Factor.	K_b (g.-mol. kg.$^{-1}$).
0·061	—	9·883	—	—	—	—
,,	0·03106	9·577	0·306°	0·314°	1·69	0·17
,,	0·07341	9·165	0·718	0·735	1·66	0·20
,,	0·1167	8·769	1·114	1·137	1·62	0·20
,,	0·1506	8·464	1·419	1·444	1·59	0·20
,,	0·1828	8·175	1·708	1·736	1·58	0·22
					Mean	0·20

(2.6) *The Solute Nitromethane.*—This parent nitro-compound has been examined in order to ascertain whether aliphatic as well as aromatic nitro-compounds display basic properties in sulphuric acid. No study of the cryoscopic behaviour of any aliphatic nitro-compound in sulphuric acid seems to have been recorded, apart from the original investigation of nitromethane by Hantzsch, who concluded that it dissolved without essential change.

Some measurements for nitromethane are recorded in Table V. From them, ν-factors and the basicity constant

$$K_b(CH_3{\cdot}NO_2) = [CH_3{\cdot}NO_2H^+][HSO_4^-]/[CH_3{\cdot}NO_2]$$

are calculated, in the same way as for 2 : 4 : 6-trinitrotoluene. It is obvious from the ν-factors that, in 0·1—0·2 molal concentration in the slightly aqueous sulphuric acid employed as solvent, about 8% of the nitromethane is ionised. From the basicity constant, $K_b = 0{\cdot}0055$, it can be computed that, in 0·1 molal concentration in anhydrous sulphuric acid, about 21% would be ionised.

TABLE V.

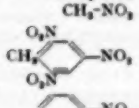
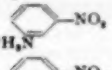
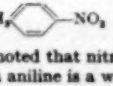
Freezing points of solutions of nitromethane in sulphuric acid (Expt. 33).

Molality of water (m_0).	Molality of $CH_3{\cdot}NO_2$ (Δm_2).	F. p. (° c.).	Depressions. $\Delta\theta_1$.	Depressions. $\Delta\theta_2$.	ν-Factors.	K_b (g.-mol. kg.$^{-1}$).
0·060	—	9·866	—	—	—	—
,,	0·0380	9·625	0·249°	0·250°	1·09	0·0059
,,	0·0764	9·371	0·495	0·498	1·08	0·0055
,,	0·1043	9·192	0·674	0·678	1·07	0·0049
,,	0·1352	8·992	0·874	0·879	1·07	0·0051
,,	0·1519	8·879	0·987	0·992	1·07	0·0051
,,	0·1844	8·668	1·198	1·204	1·08	0·0062
					Mean	0·0055

(2.7) *Relative Basicities of Nitro-compounds.*—The information that we have obtained concerning the basicities of the nitro-compounds studied is summarised in Table VI.

TABLE VI.

Basicities of nitro-compounds in sulphuric acid.

Compound.	K_b (g.-mol. kg.$^{-1}$).	Approx. % ionisation (0·1 molal in anhyd. H_2SO_4).
$CH_3{\cdot}NO_2$	$5{\cdot}5 \times 10^{-3}$	21
	$6{\cdot}7 \times 10^{-3}$	23
	$1{\cdot}4 \times 10^{-3}$	31
	$2{\cdot}9 \times 10^{-3}$	41
	$2{\cdot}0 \times 10^{-2}$	73

It will be noted that nitrobenzene is a stronger base than nitromethane in solvent sulphuric acid, although aniline is a weaker base than methylamine in water. The inversion, as between aliphatic and aromatic analogues, may plausibly be referred to the theory that the mesomeric effect in the aromatic series displaces the electron distribution oppositely for nitro-compounds and for amines, *viz.*, towards the nitro-group in nitrobenzene and away from the amino-group in aniline.

The present work establishes conclusively that the nitro-group possesses a definite, although small, basicity in sulphuric acid; this, as would be expected, is increased when the attached residue is electron-repelling, and decreased when it is electron-attracting. The relatively small basicity of the nitro-group, despite its two negatively charged oxygen atoms, is, no doubt, to be attributed to the large amount of resonance energy which must be lost on the addition of the proton.

It is of some interest that the pale yellow colour of nitrobenzene and of *p*-nitrotoluene is considerably intensified on dissolution in sulphuric acid, whereas solutions of nitromethane in sulphuric acid, and the pure substance, are colourless. The enhanced colour of the aromatic

compounds in sulphuric acid is presumably to be associated with the increased importance, in their ions, of structures with a positive charge situated in the aromatic nucleus, *e.g.*,

(3) *Basicity of Sulphonyl Compounds in Sulphuric Acid.*

(3.1) *Previous Investigations.*—The original object of the experiments reported below was to discover whether sulphonic acids, which have been extensively employed in the study of effects due to the medium on rates of nitration in sulphuric acid solvents, behave as bases towards sulphuric acid. The enquiry was extended to include sulphones for a reason which will appear in Section 4.

The only previous cryoscopic investigation of sulphonic acids in solvent sulphuric acid is that of Hantzsch (*Z. physikal. Chem.*, 1908, **65**, 41), who examined benzenesulphonic acid, *m*-nitrobenzenesulphonic acid, and *p*-toluenesulphonic acid. In each case he employed the sodium salt of the sulphonic acid as the added solute, but made allowance for that part of the freezing-point depression which was attributable to the formed sodium hydrogen sulphate. He found that the depressions due to benzenesulphonic acid, and to *m*-nitrobenzenesulphonic acid, were approximately those to be expected of the non-ionised molecule in either case. On the other hand, the depression given by *p*-toluenesulphonic acid was considerably greater than that of the non-ionised molecule. The experiments were not sufficiently precise to detect with certainty a limited amount of ionisation of the free sulphonic acid, and therefore the question of the reality of such ionisation has been reinvestigated in the examples of sodium benzenesulphonate and sodium *p*-toluenesulphonate. There is no previous record of cryoscopic experiments on sulphones in sulphuric acid.

(3.2) *The Solute Sodium Benzenesulphonate* (*Basicity of Benzenesulphonic Acid*).—Some measurements of the depression, produced by sodium benzenesulphonate, of the freezing point of sulphuric acid are given in Table VII. It is necessary to correct the observed freezing-point depressions ($\Delta\theta_1$) for the repression of ionisation of the water, and of autoprotolysis in the solvent, by the hydrogen sulphate ions which are formed in the solvolysis of the sodium benzenesulphonate. This has been done by the method outlined in Part I. From the corrected depressions ($\Delta\theta_2$), ν-factors have been calculated from the general formula (equation 5 in Part I), with the substitutions $s_2 = 4$ and $\nu_2 = 3$ in the correction factor. The value of s_2 is based on the reasonable assumptions that sodium hydrogen sulphate, like potassium hydrogen sulphate, has a solvation number of 2 (cf. Part I), and that a non-ionised benzenesulphonic acid molecule forms a hydrogen-bonded compound with one molecule of sulphuric acid, *i.e.*, has the solvation number 1, like nitrobenzene. It appears that under the conditions of these experiments, which involve the presence of an excess of hydrogen sulphate ion, the benzenesulphonic acid is ionised as a base * to the extent of about 13%.

TABLE VII.

Freezing points of solutions of sodium benzenesulphonate in sulphuric acid (Expt. 61).

Molality of water (m_s).	Molality of $C_6H_5{\cdot}SO_3Na$ (Δm_2).	F. p. (° c.).	Depressions. $\Delta\theta_1$.	Depressions. $\Delta\theta_2$.	ν-Factor.	K_b (g.-mol. kg.$^{-1}$).
0·048	—	9·999	—	—	—	—
,,	0·00667	9·876	0·123°	0·126°	3·10	0·007
,,	0·01441	9·727	0·272	0·280	3·20	0·016
,,	0·02570	9·522	0·477	0·490	3·14	0·012
,,	0·03946	9·268	0·731	0·747	3·11	0·011
,,	0·04789	9·108	0·891	0·909	3·10	0·011
					Mean	0·011

The basicity constant of benzenesulphonic acid, as defined by the expression

$$K_b(Ph{\cdot}SO_3H) = [Ph{\cdot}SO_3H_2^+][HSO_4^-]/[Ph{\cdot}SO_3H]$$

with the concentrations in molalities, has been calculated from the formula

$$K_b = [(\nu - 2)(\nu - 3)\Delta m_2 + (\nu - 3)m_1]/(4 - \nu)$$

* The idea that it might be ionised as an acid is excluded by comparisons with other acids (even perchloric acid is very weak—cf. Part VI), and by the consideration that a *p*-methyl substituent increases the ionisation (Section 2.3), as it should increase basic ionisation, but contrary to the way in which it should influence acidic ionisation.

The values are in the Table. From the mean value of K_b it can be calculated that benzenesulphonic acid would be ionised to the extent of about 28% in a 0·1 molal solution in anhydrous sulphuric acid.

(3.3) *The Solute Sodium* p-*Toluenesulphonate* (*Basicity of* p-*Toluenesulphonic Acid*.)—Some new measurements have been made of the freezing-point depression produced by sodium *p*-toluenesulphonate in sulphuric acid. The results are given in Table VIII. Values of the ν-factor and of K_b have been calculated in exactly the same way as for sodium benzenesulphonate. The results show that *p*-toluenesulphonic acid is appreciably more basic than benzenesulphonic acid. It is ionised to the extent of about 22% under the conditions of the experiment, and, as can be calculated from the mean K_b value, about 40% of the acid would be ionised in a 0·1 molal solution in anhydrous sulphuric acid.

TABLE VIII.

Freezing points of solutions of sodium p-*toluenesulphonate in sulphuric acid* (Expt. 109).

Molality of			Depressions.			
water (m_a).	p-$CH_3{\cdot}C_6H_4{\cdot}SO_3Na$ (Δm_b).	F. p. (° c.).	$\Delta\theta_1$.	$\Delta\theta_2$.	ν-Factor.	K_b (g.-mol. kg.$^{-1}$).
0·053	—	9·943	—	—	—	—
,,	0·05150	9·654	0·289°	0·296°	3·23	0·021
,,	0·02844	9·396	0·547	0·559	3·24	0·027
,,	0·04036	9·174	0·769	0·784	3·19	0·023
,,	0·05208	8·936	1·007	1·024	3·22	0·032
,,	0·06073	8·598	1·345	1·367	3·20	0·025
					Mean	0·026

(3.4) *The Solute Diphenyl Sulphone*.—For the purpose of comparison with the compounds discussed in the two preceding sections, some measurements have been made on diphenyl sulphone, and the results are given in Table IX. Freezing-point depressions have been corrected as in the preceding examples. The ν-factors in the Table have been calculated from the general formula (equation 5 in Part I) with $s_b = 1$ and $\nu_b = 1$ substituted in the nearly-unit correction factor. We have assumed, as we have for benzene- and toluene-sulphonic acids, that the non-ionised molecule of the solute diphenyl sulphone has a solvation number of unity. The basicity constant of diphenyl sulphone, as defined by the expression

$$K_b(Ph_2SO_2) = [Ph_2SO_2H^+][HSO_4^-]/[Ph_2SO_2]$$

with the concentrations in molalities, has been calculated from the formula

$$K_b = \{(\nu - 1)^2\Delta m_b + (\nu - 1)m_a\}/(2 - \nu)$$

The values obtained are recorded in the Table. It can be seen that, in the slightly aqueous sulphuric acid employed in the experiment, about 19% of the diphenyl sulphone is ionised. From the mean value of K_b it can be calculated that about 33% of it would be ionised in anhydrous sulphuric acid.

TABLE IX.

Freezing points of solutions of diphenyl sulphone in sulphuric acid (Expt. 107).

Molality of			Depressions.			
water (m_a).	Ph_2SO_2 (Δm_b).	F. p. (° c.).	$\Delta\theta_1$.	$\Delta\theta_2$.	ν-Factor.	K_b (g.-mol. kg.$^{-1}$).
0·060	—	9·897	—	—	—	—
,,	0·01050	9·822	0·075°	0·076°	1·21	0·015
,,	0·03045	9·682	0·215	0·218	1·20	0·015
,,	0·05330	9·525	0·372	0·377	1·18	0·014
,,	0·07990	9·324	0·573	0·580	1·21	0·019
,,	0·1139	9·110	0·787	0·796	1·16	0·014
,,	0·1383	8·932	0·965	0·976	1·17	0·016
					Mean	0·016

(4) *Basicity of Sulphuryl Compounds in Sulphuric Acid.*

(4.1) *Previous Investigations*.—The contrast between the cryoscopic properties in solvent sulphuric acid of the non-basic halogen-sulphuryl compounds, which were used for the determination of the cryoscopic constant of sulphuric acid, as described in Part I (*J.*, 1950, 2473), and those of the definitely basic aryl-sulphonyl compounds, treated in the preceding Section,

suggested that some examination ought to be made of the esters of sulphuric acid, which, on general electrostatic grounds, would be expected to exhibit an intermediate degree of basic character. The normal esters of sulphuric acid appear, however, to be unsuitable solutes for cryoscopic study in sulphuric acid, dimethyl sulphate having given evidence of partial decomposition in that solvent (cf. Part I). On the other hand, the alkyl-sulphuric acids (alkyl hydrogen sulphates) are well known to be stable in sulphuric acid, in excess of which they are rapidly and completely formed from the simpler alcohols. Accordingly ethylsulphuric acid ($EtHSO_4$) was considered a suitable subject for the present study.

Advantage was taken of the reaction by which ethyl alcohol is converted into ethylsulphuric acid for the convenience of being able to introduce the latter through the medium of a weighed solute of easily controlled purity. So far as is known, the conversion of ethyl alcohol into ethylsulphuric acid by a large excess of sulphuric acid is quantitative. Even if it were not quite quantitative, no advantage would be gained by adding weighed ethylsulphuric acid, or one of its salts, since a similar solution would result from the setting up of an esterification equilibrium, whether the initially added substance were the ester or the alcohol. Actually, the cryoscopic results themselves indicate that the formation of the ester is quantitative.

The cryoscopic behaviour of a number of aliphatic and aromatic alcohols has been investigated by Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257; 1908, **65**, 41) and by Oddo and Scandola (*Gazzetta*, 1909, **39**, II, 1). They showed that methyl and ethyl alcohols gave an approximately three-fold depression of the freezing point of sulphuric acid; and this is consistent with an extensive, or possibly a complete, conversion of the alcohol into the corresponding alkylsulphuric acid and water, *e.g.*,

$$[C_2H_5{\cdot}OH + 2H_2SO_4 = C_2H_5{\cdot}SO_4H + H_3O^+ + HSO_4^-$$

Oddo and Scandola obtained this result for these two, and some other, primary alcohols; but with a number of secondary and tertiary alcohols they obtained depressions which varied, according to the compound, from two to three times that of a non-electolyte. These secondary and tertiary alcohols, unlike methyl and ethyl alcohol, give yellow solutions in sulphuric acid, and, on pouring them into ice-water, unsaturated hydrocarbons are obtained. In disagreement with Hantzsch, these authors found that triphenylcarbinol gave a four-fold, and not a three-fold, freezing-point depression, a result which has since been confirmed by Hammett and Deyrup (*loc. cit.*). This indicates that triphenylmethylsulphuric acid is completely ionised in sulphuric acid into the triphenylmethyl cation and the hydrogen sulphate ion, or in other words, that triphenylcarbinol is fully ionised according to the equation

$$Ph_3C{\cdot}OH + 2H_2SO_4 = Ph_3C^+ + H_3O^+ + 2HSO_4^-$$

Hantzsch also investigated methyl- and ethyl-sulphuric acids by measuring the depression produced by their sodium salts, and allowing for the depression caused by the sodium hydrogen sulphate. His results showed that these two alkylsulphuric acids are little, if at all, ionised in sulphuric acid.

(4.2) *The Solute Ethyl Alcohol* (*Basicity of Ethylsulphuric Acid*).—The observed freezing points of solutions of ethyl alcohol in sulphuric acid are given in Table X. The freezing-point depressions $\Delta\theta_1$ are corrected for the repression of autoprotolysis by the formed water. The *v*-factors are calculated by means of the general equation, with the substitutions $s_2 = 2$ and $v_2 = 3$ in the correction factor. These substitutions take care of a previous conclusion that the solvation number of hydroxonium hydrogen sulphate is unity.

TABLE X.

Freezing points of solutions of ethyl alcohol in sulphuric acid.

Molality of EtOH		F. p.	Depression.		*v*-	Molality of EtOH		F. p.	Depression.		*v*-
(m_2).	(Δm_2).	(°C.).	$\Delta\theta_1$.	$\Delta\theta_2$.	Factor.	(m_2).	(Δm_2).	(°C.).	$\Delta\theta_1$.	$\Delta\theta_2$.	Factor.
Expt. No. 58. Molality of water (m_1) = 0·027.						Expt. No. 59. Molality of water (m_1) = 0·046.					
—	—	10·207	—	—	—	—	—	10·024	—	—	—
0·0160	—	10·028	—	—	—	0·0127	—	9·815	—	—	—
0·0213	—	9·839	—	—	—	0·0244	0·0117	9·610	0·205°	0·210°	2·96
0·0326	0·0113	9·640	0·199°	0·205°	3·00	0·0333	0·0206	9·449	0·366	0·373	2·99
0·0414	0·0201	9·483	0·356	0·365	2·99	0·0421	0·0294	9·295	0·520	0·529	2·97
0·0572	0·0359	9·207	0·632	0·645	2·96	0·0507	0·0380	9·145	0·670	0·682	2·95
				Mean	2·98					Mean	2·97

A completed single-stage esterification of the alcohol, according to the reaction

$$C_2H_5{\cdot}OH + 2H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_3O^+ + HSO_4^-$$

would require $\nu = 3$. A completed two-stage esterification, according to the equation

$$2C_2H_5{\cdot}OH + 3H_2SO_4 = (C_2H_5)_2SO_4 + 2H_3O^+ + 2HSO_4^-$$

would require $\nu = 2{\cdot}5$. These equations require correction, since, as is shown in Part II (*J.*, 1950, 2493), the ions of water will partly reassociate, setting up the equilibrium

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

It was established in Part II that, owing to this balanced reaction, the ν-factor for water is not 2, but has a mean value of 1·89 over the range of concentrations which it has been found convenient to use in the present cryoscopic work. Thus the theoretical ν-factor for no esterification is 1·00, for a quantitative one-stage esterification it has the mean value 2·89, and for a complete two-stage esterification it has the smaller value 2·39. Thus, when the conversion into ethylsulphuric acid is quantitative, the ν-factor should reach a maximum of 2·89, or, more accurately, 2·92, allowance here being made for the repression or solvent autoprotolysis by the formed water. The difference between the expected maximum of 2·92 and the observed value of 2·97 means that, over the range of concentrations employed, ethylsulphuric acid has a ν-factor of 1·05. There are two possible interpretations * of this result: either ethylsulphuric acid behaves as a simple but fairly weak base, ionising according to the equation

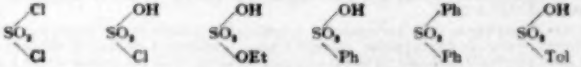
$$C_2H_5{\cdot}SO_4H + H_2SO_4 = C_2H_5{\cdot}SO_4H_2^+ + HSO_4^-,$$

or it dissociates to a limited extent into the ethyl cation and a hydrogen sulphate ion, thus

$$C_2H_5{\cdot}SO_4H = C_2H_5^+ + HSO_4^-$$

The known formation of the triphenylmethyl cation from triphenylcarbinol, and the indication of the existence of carbon cations in solutions of secondary and tertiary alcohols in sulphuric acid, provide some support for the formation of the ethyl cation in small amounts in solutions of ethyl alcohol in sulphuric acid. However, if this latter reaction does not occur, and ethylsulphuric acid behaves simply as a base, then we must conclude that it is a weak base, somewhat weaker than benzenesulphonic acid.

(4.3) *Relative Basicities of Sulphonyl and Sulphuryl Compounds.*—Having regard to data recorded in Part I of this series, and in Section 2 of this paper, the above measurements can be considered to complete a constitutionally graded series, in which the group $-SO_2-$ is bonded, in $R'R''SO_2$, to various groups R, satisfying the conditions that they do not contain atoms intrinsically more basic than the oxygen atoms of the sulphone group itself. In practice this condition limits the groups R to hydrocarbon radicals, hydroxyl or alkoxyl groups, and halogen atoms. The following series (Tol = *p*-tolyl) appears to represent an order of increasing basicity:



It appears, as seems reasonable, that increasing basicity is observed when either variable group becomes less electronegative, *i.e.*, when there is a substitution of any group by another standing to its right in the following electropolar series: Cl, OR, Ph, Tol.

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University College, London, W.C.1. [*Received, December 17th*, 1949.]

* It is considered extremely unlikely that ethylsulphuric acid could be ionised as an acid: such an explanation would require it to be a much stronger acid than sulphuric acid, comparable in strength, indeed, to perchloric acid (though this is still a weak acid in solvent sulphuric acid). This would seem to be improbable on electrostatic grounds, and it would be contrary to the general regularities, discussed in Part VI, concerning the strengths of oxy-acids.

504. *Cryoscopic Measurements in Nitric Acid. Part I. The Solutes Dinitrogen Pentoxide and Water. The Self-dissociation of Nitric Acid.*

By R. J. Gillespie, E. D. Hughes, and C. K. Ingold.

The freezing-point diagram of the system N_2O_5–H_2O has been studied over a range of compositions in the neighbourhood of that of HNO_3. From the form of the freezing-point curve on the dinitrogen pentoxide side of the nitric acid maximum, it is concluded that dinitrogen pentoxide in nitric acid is completely dissociated into nitronium and nitrate ions, which are solvated with a total of 4 molecules of nitric acid. From the form of the curve on the water side of the maximum, it is deduced that water in dilute solution in nitric acid is entirely non-ionised, but that each water molecule is solvated with 2 molecules of nitric acid. From the form, and the amount, of the rounding of the freezing-point maximum, it is concluded that nitric acid is considerably self-dissociated, the principal process being the ionic self-dehydration,

$$2HNO_3 = NO_2^+ + NO_3^- + H_2O$$

It is estimated that, in analytically anhydrous nitric acid at −40°, some 3·4% of the material is dissociated to give 1·2% of nitronium ion, 1·7% of nitrate ion, and 0·5% of water. A further 10% of the nitric acid has to be pictured as being bound in solvates of the self-dissociation products.

(I) *Methods and Results.*

(1.1) *Objects and Background.*—The motive of the present work was to prepare the ground for a general investigation of the cryoscopic behaviour of solutes in solvent nitric acid. The cryoscopic constant of nitric acid having been established by the calorimetric measurements of Forsyth and Giauque (cf. Section 1.3), the primary necessity was to study the self-dissociation of the solvent, and the behaviour of those solutes which are involved in the self-dissociation. This involves measurement of the freezing-point curve of the binary system N_2O_5–H_2O for compositions in the neighbourhood of HNO_3. Such measurements, and the conclusions to be drawn from them, form the subject of the present paper. The work is recorded at this time, because of its close connection with the chemical and physical studies on nitric acid described in several of the accompanying papers (particularly *J.*, 1950, 2400 and paper no. 510).

The only previously published cryoscopic investigations on solutions in nitric acid are those of Pickering (*J.*, 1893, **63**, 436) and of Berl and Saenger (*Monatsh.*, 1929, **54**, 1036) on the system N_2O_5–HNO_3, and of Kuster and Kremann (*Z. anorg. Chem.*, 1904, **41**, 1) on the system HNO_3–H_2O. In both these studies, the freezing points were measured somewhat approximately at widely spaced intervals of composition.

(1.2) *Apparatus and Experimental Procedure.*—The freezing-point cell was the same as that used for the measurements with sulphuric acid; and, in general, the same procedure for making a freezing-point measurement was adopted. The external bath, in which the cryoscope, surrounded by an air-jacket, was supported, consisted of a large Dewar vessel containing alcohol, which could be cooled by pumping alcohol at −60° to −70° through an immersed metal coil, and could be heated electrically when necessary. During a determination, the temperature of the bath was kept constant to ±0·2°, at about 2° below the freezing point, by means of a bimetallic-strip regulator, which controlled the heater, and the pump motor, through a relay.

It was not found possible to seed the solute by touching the outside of the cryoscope with a piece of solid carbon dioxide; and, in consequence, the more direct method of seeding by adding a very small amount of the solid solvent was used. A small quantity of nitric acid was frozen inside a narrow tube, and then pushed out inside the cryoscope so that it fell directly into the solution.

Nitric acid was weighed by means of a weight burette provided with a vacuum jacket which, by preventing condensation on the outside, enabled the nitric acid to be weighed while it was kept below −30°. At these temperatures no appreciable decomposition appeared to take place, whereas at room temperature the acid soon acquired a detectable yellow colour.

Weighed amounts of water were added to the acid by means of a weight pipette. When investigating dinitrogen pentoxide, however, the solid solute was not added in separate weighed portions to the nitric acid, because of experimental difficulties. Instead, the cryoscope was charged initially with a solution of dinitrogen pentoxide in nitric acid, and the small weighed amounts of water were added. The solution of dinitrogen pentoxide in nitric acid was prepared by distilling the dinitrogen pentoxide in a stream of ozonised oxygen into nitric acid cooled to −40°. By this means, colourless solutions containing quite large amounts of dinitrogen pentoxide could readily be prepared, although attempts to add solid dinitrogen pentoxide directly to the liquid acid always resulted in a yellow solution, probably owing to the heat evolved. No attempt was made to prepare solutions of dinitrogen pentoxide with compositions accurately controlled by weighing, or to estimate the compositions of solutions by analysis. The compositions were found from the total amounts of water that it was necessary to add in order to reach the maximum freezing point, *i.e.*, the composition HNO_3.

A correction for supercooling, δT, was added to all the observed freezing points:

$$\delta T = (C_f^2/\Delta H_f')S = 0{\cdot}011S\theta$$

where S is the amount of supercooling, and θ the total depression of the freezing point. The values of the heat capacity of liquid nitric acid, C_p^l, and of the heat of fusion of nitric acid, ΔH_f^l, that are employed in calculating the above numerical factor, are given in Section 1.3.

(1.3) *Equation for the Freezing-point Depression.*—We shall assume that, in the range of concentrations with which we are concerned, solutions in nitric acid can be regarded as behaving ideally. Suppose that one molecule of a solute A reacts with s molecules of nitric acid to produce a total of ν dissolved ions and non-ionised molecules, thus :

$$A + sHNO_3 = pP + qQ + rR + \ldots$$

$$p + q + r + \ldots = \nu$$

If m_2 is the molality of the solute A, and m_1 the molality of the nitric acid, then the change $\Delta\theta$ in the freezing-point depression, caused by a change Δm_2 in the molality of the solute A, is given by the equation (cf. *J.*, 1950, **2478**) :

$$\frac{\Delta\theta}{\Delta m_2} = \frac{RT_0^2}{m_1\Delta H_f^0}\left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_f^0}\right)\bar{\theta}\right\}\left\{1 + \frac{(2s - \nu)\bar{m}_2}{m_1}\right\}$$

Here, $\bar{\theta}$ is the mean depression, and $\bar{m}_2$ the mean molality of the solute A, over the interval of composition to which $\Delta\theta$ and Δm_2 refer.

TABLE I.

Freezing points of solutions of water and dinitrogen pentoxide in nitric acid.

Added H_2O.	Weights (g.). Solution.	Solute.	HNO_3.	Molality of solute.	F. p. (° c.).	Depression ($\Delta\theta$).
***Expt. No.* 14 :**		N_2O_5.		N_2O_5.		
—	102·70	2·298	100·40	0·212	−41·87	0·13°
0·288	102·99	0·570	102·42	0·052	41·78	0·04
		H_2O.		H_2O.		
0·281	103·27	0·186	103·09	0·100	41·74	0·00
0·285	103·56	0·471	,,	0·253	41·84	0·10
0·690	104·25	1·161	,,	0·625	42·34	0·60
0·825	105·07	1·986	,,	1·068	43·21	1·47
0·708	105·78	2·694	,,	1·450	44·14	2·40
0·622	106·40	3·316	,,	1·786	45·13	3·39
***Expt. No.* 15 :**		N_2O_5.		N_2O_5.		
—	117·96	6·578	110·38	0·552	−42·96	1·15
0·182	118·14	5·466	112·67	0·449	42·59	0·78
0·168	118·31	4·458	113·85	0·363	42·27	0·46
0·190	118·50	3·318	115·18	0·267	42·07	0·26
0·199	118·70	2·124	116·58	0·168	41·93	0·12
0·198	118·90	0·936	117·96	0·073	41·84	0·03
		H_2O.		H_2O.		
0·300	119·20	0·144	119·06	0·067	41·81	0·00
0·193	119·39	0·337	,,	0·157	41·83	0·02
0·179	119·57	0·516	,,	0·241	41·85	0·04
***Expt. No.* 16 :**		N_2O_5.		N_2O_5.		
—	86·72	12·098	74·62	1·501	−50·57	8·76
0·402	87·12	9·682	77·44	1·158	47·40	5·59
0·141	87·26	8·836	78·42	1·044	46·37	4·56
0·109	87·37	8·182	79·19	0·957	45·62	3·81
0·084	87·45	7·678	79·77	0·891	45·19	3·38
0·081	87·53	7·192	80·34	0·829	44·64	2·83
0·033	87·56	6·994	80·57	0·804	44·55	2·74
0·085	87·65	6·484	81·17	0·740	44·05	2·24
0·113	87·76	5·806	81·95	0·656	43·55	1·74
0·087	87·85	5·264	82·59	0·589	43·19	1·38
***Expt. No.* 19 :**		H_2O.		H_2O.		
—	88·95	—	88·93	—	−41·78	—
1·388	90·24	1·388	,,	0·867	42·84	1·06
1·117	91·36	2·505	,,	1·565	44·76	2·98
0·894	92·25	3·399	,,	2·123	46·55	4·77
0·786	93·04	4·185	,,	2·614	48·35	6·57

The values of the cryoscopic constant $k_f = RT_0^2/m_1\Delta H_f^l$, and of the factor $\{(2/T_0) - (\Delta C_p/\Delta H_f^l)\}$ have been calculated from the following data of Forsyth and Gianque (*J. Amer. Chem. Soc.*, 1942, **64**, 48) : $T_0 = -41{\cdot}65°$ c. $= 231{\cdot}51°$ K., $\Delta H_f^l = 2503$ cal. g.-mol.$^{-1}$, and the extrapolated values $C_p^l(-41{\cdot}7°) = 26{\cdot}74$ cal. g.-mol.$^{-1}$ deg.$^{-1}$, and $C_p^s(-41{\cdot}7°) = 16{\cdot}56$ cal. g.-mol.$^{-1}$ deg.$^{-1}$. We thus find $k_f = 2{\cdot}68$ deg. g.-mol.$^{-1}$ kg., and $\{(2/T_0) - (\Delta C_p/\Delta H_f^l)\} = 0{\cdot}0045$ deg.$^{-1}$. The value of m_1 is 15·87 g.-mol. kg.$^{-1}$. Hence we obtain the following freezing-point equation :

$$\Delta\theta/\Delta m_2 = 2{\cdot}68s\{1 - 0{\cdot}0045\bar{\theta} + (2s - \nu)\overline{m}_2/15{\cdot}87\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(1.4) *Results.*—The results obtained in several experiments in which the freezing point was measured with the addition of successive small weighed amounts of water to a solution of dinitrogen pentoxide in nitric acid, or to pure nitric acid, are given in Table I.

Forsythe and Gianque (*loc. cit.*) found the freezing point of nitric acid to be $-41{\cdot}65°$. We have found freezing points of different samples of acid ranging from $-41{\cdot}71°$ to $-41{\cdot}81°$. We have assumed that these slightly low values are due to a small amount of decomposition of the acid, because samples with a freezing point appreciably lower than $-41{\cdot}7°$ had a just perceptible yellow colour. Freezing-point depressions for the solutes water and dinitrogen pentoxide have been calcultated from the observed maximum freezing point of the acid used, and not from the freezing point of the pure acid.

The experimental results are shown graphically in Fig. 1, in association with calculated curves for an ideal non-electrolyte, and an ideal binary electrolyte, with various solvation numbers s. The theoretical freezing-point depressions, from which these curves are drawn, are given in Tables II and III. They were calculated from equation (1).

TABLE II.

Calculated freezing-point depressions for solution of a non-electrolyte in nitric acid.

		Depressions.					
		$s = 0$.		$s = 1$.		$s = 2$.	
Molality of solute, m_2.	Δm_2.	$\Delta\theta_0$.	θ_0.	$\Delta\theta_1$.	θ_1.	$\Delta\theta_2$.	θ_2.
0·25	0·25	0·663°	0·663°	0·674°	0·674°	0·685°	0·685°
0·75	0·50	1·291	1·954	1·377	2·051	1·454	2·139
1·25	,,	1·241	3·195	1·407	3·458	1·573	3·712
1·75	,,	1·193	4·388	1·439	4·897	1·682	5·394
2·25	,,	1·145	5·533	1·470	6·367	1·793	7·187
2·75	,,	1·097	6·630	1·501	7·868	1·901	9·088
3·25	,,	1·051	7·681	1·531	9·399	2·005	11·093

TABLE III.

Calculated freezing-point depressions for solutions of a binary electrolyte in nitric acid.

		Depressions.					
		$s = 0$.		$s = 2$.		$s = 4$.	
Molality of solute, m_2.	Δm_2.	$\Delta\theta_0$.	θ_0.	$\Delta\theta_2$.	θ_2.	$\Delta\theta_4$.	θ_4.
0·25	0·25	1·313°	1·313°	1·357°	1·357°	1·398°	1·398°
0·75	0·50	2·483	3·796	2·606	4·163	3·140	4·538
1·25	,,	2·290	6·086	2·940	7·093	3·557	8·095
1·75	,,	2·104	8·190	3·050	10·140	3·897	11·992

(2) *Discussion.*

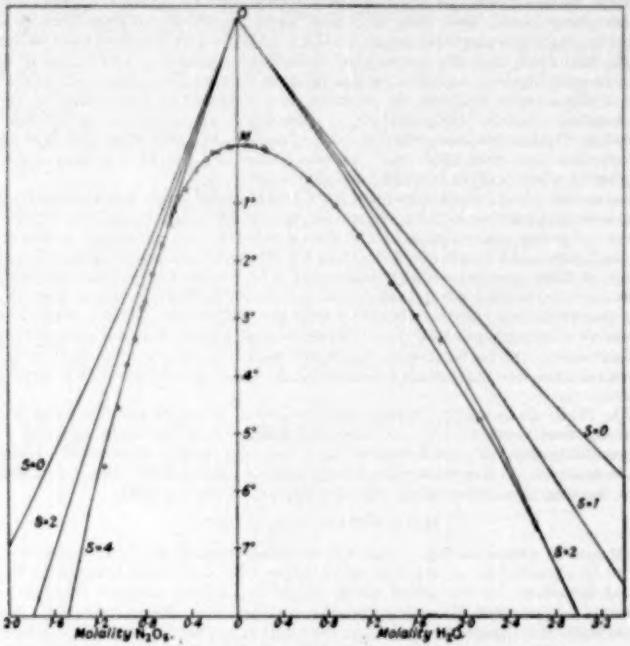
(2.1) *General Character of the Freezing-point Curve.*—It is immediately obvious from Fig. 1 that there is a considerable difference between the effects of water and dinitrogen pentoxide on the freezing point of nitric acid. The slope of the dinitrogen pentoxide branch of the freezing-point curve is approximately twice as great as that of the water branch, and this indicates that a molecule of dinitrogen pentoxide produces approximately twice as many solute particles as does a molecule of water. The other obvious feature of this freezing-point curve is the very rounded character of the maximum at the composition HNO_3, a clear indication that nitric acid is considerably self-dissociated.

The existence of this large self-dissociation makes it necessary to study solutions at much higher concentrations, and with correspondingly larger freezing-point depressions, than were used in the study of solutions in sulphuric acid (*J.*, 2473, *et seq.*). It is therefore important to know how far solutions in nitric acid can be regarded as behaving ideally in the concentration range

investigated. Unfortunately we have no information about this, except the present freezing-point data, which indicate that the principal deviation from ideal behaviour is that due to solvation, although the possibility of some deviation due to interionic attraction is not excluded. One can, as we shall see, account very satisfactorily for the observed deviations from ideal behaviour by attributing small and plausible solvation numbers to the various dissolved species, completely neglecting any possible deviations due to interionic attractions or other causes.

FIG. 1.

Freezing points of the system dinitrogen pentoxide–water at compositions near that of nitric acid. Of the nearly straight lines which meet at the point O, those on the right are theoretical freezing-point curves for an ideal non-electrolyte with solvation numbers s = 0, 1, 2; and those on the left are theoretical curves for an ideal binary electrolyte with (total) solvation numbers s = 0, 2, 4.



(2.2) *The Dinitrogen Pentoxide Branch of the Freezing-point Curve.*—The slope of the freezing-point curve for dinitrogen pentoxide shows that it forms at least two ions in solution in nitric acid. A resonable mode of ionisation, giving two ions, is the following:

$$N_2O_5 = NO_2^+ + NO_3^-$$

and it is, indeed, difficult to formulate any other mode of ionisation, or any mode at all which would give more than two ions. As can be seen from Fig. 1, the observed slope is somewhat greater than that to be expected for a non-solvated binary electrolyte, but it can be adequately explained by assuming that the total solvation number of the formed ions is 4.

This interpretation of the freezing-point data is in agreement with other information about solutions of dinitrogen pentoxide in nitric acid. It is shown in an accompanying paper (Ingold and Millen, *J.*, 1950, paper no. 510) that the effect on the Raman spectrum of adding, say, 6% of dinitrogen pentoxide to nitric acid is to superpose, on the normal spectrum of nitric acid, the spectra of the nitronium ion and the nitrate ion, but to produce no other spectral appearance, and, in particular, no trace of the known spectrum of molecular dinitrogen pentoxide. This is an

independent demonstration that dinitrogen pentoxide, at concentrations of this order (0·6 molal), is a strong electrolyte, consisting only of nitronium and nitrate ions. The formation of these ions explains the large increase of electrical conductivity which is observed on adding dinitrogen pentoxide to nitric acid (Berl and Saenger, *loc. cit.*); whilst the strong solvation of the ions accounts for their lack of tendency to associate, as is indicated by the negligible effect on the total vapour pressure of adding quantities, even up to 23%, of dinitrogen pentoxide to nitric acid at 0° (*idem, ibid.*).

One would certainly expect the nitrate ion to be strongly solvated in nitric acid. A number of compounds between ammonium, or alkali-metal, nitrates and nitric acid have been described (Ditte, *Compt. rend.*, 1879, **89**, 567; *Ann. Chim. Phys.*, 1879, **18**, 320; Wells and Metzger, *Amer. Chem. J.*, 1901, **26**, 272; Groschuff, *Ber.*, 1904, **37**, 1486; *Z. anorg. Chem.*, 1904, **40**, 1): they have the general formulæ $MNO_3.HNO_3$ and $MNO_3.2HNO_3$. Chédin, Leclerc, and Vandoni have found (*Compt. rend.*, 1947, **225**, 734) that the exothermicity of dissolution of potassium nitrate in nitric acid is remarkably large (6 kcals.). Chédin and Vandoni have shown (*Compt. rend.*, 1948, **227**, 1232) that the lowering of the vapour pressure of nitric acid by potassium nitrate can be quantitatively explained, if it is assumed that the dissociated salt has the solvation number 2. The authors attribute the solvation to a tendency of the nitrate ion to form the hydrogen-bonded complex, $(NO_3^-)(HNO_3)_2$; and this idea of the nature of the solvation is supported by Chédin and Fénéant's discovery (*Compt. rend.*, 1949, **228**, 242) that the Raman OH-band of nitric acid near 3400 cm.$^{-1}$ becomes partly replaced by a system of several OH-stretching bands when potassium nitrate is added to nitric acid.

If we accept the value 2 for the solvation number of the nitrate ion, then the assumption of the reasonable solvation number of 2 for the nitronium ion will suffice to account for the freezing-point curve. General confirmation of the strong solvation of dinitrogen pentoxide follows from Chédin, Leclerc, and Vandoni's observation that the exothermicity of dissolution of water in a dissolution of dinitrogen pentoxide in nitric acid is very much smaller than the exothermicity of solution of water in pure nitric acid (*loc. cit.*). It follows that the destruction of dissolved dinitrogen pentoxide by hydration involves a strongly endothermic process, which can only be the desolvation of strongly solvated ions. On the whole, it seems that our interpretation of the freezing-point curve on the basis that dinitrogen pentoxide is a strong electrolyte, forming stably solvated nitronium and nitrate ions in nitric acid, is in agreement with a variety of other observations.

(2.3) *The Water Branch of the Freezing-point Curve.*—As can be seen from Fig. 1, the slope of the freezing-point curve for water is somewhat greater than that to be expected for a non-solvated non-electrolyte, but much smaller than that of a binary electrolyte. Therefore one might try to interpret the observational curve by assuming that water behaves as a weak binary electrolyte, ionising to a rather small extent according to the equation :

$$H_2O + HNO_3 = H_3O^+ + NO_3^-$$

However, it can be seen from Fig. 1 that the observed freezing-point curve agrees quite well with that to be expected for a non-electrolytic solute with a solvation number of 2, *i.e.*, with the assumed formation, by the added water, of the non-ionised complex $(H_2O)(HNO_3)_2$. It is not possible to interpret the cryoscopic observations quite unambiguously; however, a considerable body of evidence can be cited to the effect that water is very little ionised in dilute solution in nitric acid, but that, on the other hand, water is quite stably solvated by nitric acid.

Investigations of the effect of added water on the Raman spectrum of nitric acid (Chédin, *Ann. Chim.*, 1937, **8**, 295; Rao, *Indian J. Physics*, 1941, **15**, 185; Redlich and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1883) have shown that the strongest line belonging to the nitrate ion, the line at 1050 cm.$^{-1}$, remains very weak, much as it is in pure nitric acid, until about 10% by weight of water has been introduced. Even in an equimolecular mixture of nitric acid and water, containing 22% by weight of water, the proportion of material ionised, as indicated by the intensity of the nitrate ion line, is no more than 2%. It seems impossible, therefore, that the first few units % of added water could produce sufficient ions to account for the deviation of the freezing-point curve from that of a non-solvated non-electrolyte. The same conclusion follows from studies of the electrical conductivity of mixtures of nitric acid and water (Veley and Manley, *Phil. Trans.*, 1898, **191**, *A*, 365; Dalmon, *Mem. Serv. chim. de l'État*, 1943, **30**, 191). The conductivity of nitric acid containing as much as 10% by weight of water is not substantially greater than that of anhydrous nitric acid; and the addition of the first few units % of water to nitric acid causes a fall in conductivity.

The fact that water, although it forms very few ions, does form a stable solvate with solvent

nitric acid has been shown by Chédin in several ways (Chédin and Fénéant, *Compt. rend.*, 1947, **224**, 930; Chédin, Leclerc, and Vandoni, *loc. cit.*; Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722). The partial vapour pressures of water over a solution of water in nitric acid are exceedingly small at all concentrations up to 20% by weight of water. The exothermicity of dissolution of water in absolute nitric acid is very considerable (3 kcals.). The effect of adding up to 20% by weight of water to nitric acid on the Raman OH-band near 3400 cm.$^{-1}$ is gradually to replace it by a group of several bands. This shows that water, like the nitrate ion, forms with solvent nitric acid a stable hydrogen-bond complex.

The exact composition of the complex is, however, open to some doubt. The only known solid compounds of water and nitric acid are $(H_2O)_3(HNO_3)$ and $(H_2O)(HNO_3)$, and, of these, the latter at most could be of possible importance in the range of composition in which we are interested (cf. Kuster and Kremann, *loc. cit.*). Chédin, Fénéant, and Vandoni have deduced from the partial vapour pressures of water and nitric acid above their solutions that the complex $(H_2O)(HNO_3)$ is produced (*loc. cit.*). Their data refer to solutions containing from 20% to 5% by weight of water. Our freezing-point results indicate the complex to be $(H_2O)(HNO_3)_2$. However, our data relate to solutions containing from 5% to 0% by weight of water. The two conclusions are not necessarily inconsistent. The simpler solvate, probably the hydrogen-bond complex, H_3OHONO_2, is apparently rather stable; but when many nitric acid molecules are in competition for each water molecule, the latter may form a second similar bond to give the complex $H_3O(HONO_2)_2$, thus completing the co-ordination shell of its oxygen atom.

(2.4) *The Rounding of the Freezing-point Maximum.*—This feature of the freezing-point curve indicates that the self-dissociation of nitric acid is extensive. If there were no self-dissociation, the dinitrogen pentoxide and the water branch of the freezing-point curve would meet in a point, as do the theoretical curves for the two solutes. The presence of the products of self-dissociation depresses the freezing point of the pure solvent below the value it would have if it did not undergo dissociation. The addition to the pure solvent of limited amounts of either dinitrogen pentoxide or water causes a partial recombination, and therefore a disappearance, of self-dissociation products; and thus the added solutes at first exert considerably less than their normal depressing effects on the freezing point. When, however, sufficient of either solute has been added to repress the self-dissociation completely, then a further portion of the solute will exert its normal depressing effect. Thus the freezing-point curve has a rounded maximum, and only the lower portion of either branch of the curve is expected to agree with the theoretical curve for the relevant solute.

These principles have been applied in constructing Fig. 1. First, the theoretical curves were drawn. Then the experimental curve was plotted, and so placed that its maximum fell vertically beneath the origin of the theoretical curves, whilst its two branches ran as nearly as possible asymptotically to two of the theoretical curves. The interval between the origin *O* of the theoretical curves and the maximum *M* of the experimental curve is 2·20°. It represents the amount by which the products of self-dissociation of the solvent reduce its freezing point.

The simplest type of self-dissociation that we could contemplate would be the autoprotolysis

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \quad \ldots\ldots\ldots \quad (1)$$

However, the shape of the freezing-point curve shows that the self-dissociation cannot, in fact, be as simple as this. For we have seen that, whilst dissolved dinitrogen pentoxide supplies nitrate ions, small amounts of added water produce scarcely any nitrate ions. The autoprotolysis represented above should therefore be repressed effectively by added dinitrogen pentoxide, but scarcely at all by added water; and thus the freezing-point curve should be rounded on the dinitrogen pentoxide side of the maximum, but should descend sharply on the water side.

The second possibility is that the dissociation is a self-dehydration:

$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O$$

Since, as we have already seen, dinitrogen pentoxide is fully dissociated into solvated ions, whilst water, though also solvated, is scarcely ionised, the complete ionic self-dehydration can, apart from solvation, be approximately represented thus:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \quad \ldots\ldots\ldots \quad (2)$$

This equation would interpret the qualitative features of the freezing-point curve. Water is a product of this form of dissociation, as well as the ions of dinitrogen pentoxide; and hence the freezing-point curve should be rounded on both sides of the maximum, as, in fact, it is. Further,

dinitrogen pentoxide supplies two of the three products of dissociation, whereas water provides only one; hence dinitrogen pentoxide should be more effective than water in repressing the dissociation of the solvent; and hence dinitrogen pentoxide should begin to exert its full effect in depressing the freezing point at a lower concentration than should water, as, in fact, is found.

There is good evidence in the Raman spectrum of nitric acid for the presence of the three products of ionic self-dehydration. The nitronium ion is identified by the weak, but sharp, Raman line at 1400 cm.$^{-1}$, first found by Chédin in absolute nitric acid, whilst the nitrate ion has been proved to be the source of the weak frequency 1050 cm.$^{-1}$. Ingold and Millen (*J.*, 1950, paper no. 510) have estimated, from the intensities of these two lines, that absolute nitric acid is about 0·22 molal with respect to nitronium ion, and about 0·24 molal with respect to nitrate ion. The presence of water in anhydrous nitric acid is qualitatively established by Chédin and Fénéant's investigation of the high-frequency Raman bands (*Compt. rend.*, 1947, **224**, 930). In addition to the strong band at 3400 cm.$^{-1}$, representing the OH-stretching frequency of nitric acid, the absolute acid exhibits two exceedingly weak bands, at 2980 and 3550 cm.$^{-1}$, which become greatly intensified on the addition of small amounts of water, and are certainly to be attributed to a hydrogen-bonded solvate of water.

From all this evidence it seems clear that the ionic self-dehydration of nitric acid (2) is at least the chief mode of its self-dissociation. What is not clear is whether any appreciable proportion of autoprotolysis (1) occurs simultaneously. Any such autoprotolysis would produce nitric acidium ion, and would lead to a total concentration of nitrate ion in excess of that of nitronium ion. It is not an argument against the presence of the nitric acidium ion, $H_2NO_3^+$, that no evidence for it is found in the Raman spectrum. The simple hydroxonium ion, H_3O^+, in aqueous solution cannot be detected by the Raman effect; and whatever may be the cause of this might apply equally to the nitric acidium ion in nitric acid solution. Bauer suggests that the life-periods of individual hydroxonium ions are too short to produce sharp energy levels (*J. Chim. physique*, 1948, **45**, 242). Again, it is true that an approximate equivalence of nitronium and nitrate ions in absolute nitric acid has been established on the basis of Raman intensities; but the equivalence has not yet been established accurately enough to exclude the possibility that some minor but appreciable proportion, such as 10 or 15%, of the total dissociation may consist of autoprotolysis. Hughes, Ingold, and Reed have shown by a kinetic method (*J.*, 1950, 2400) that autoprotolysis is an actual step on the way to ionic self-dehydration. Thus, autoprotolysis must occur in principle, and the question now at issue is essentially the quantitative one of the proportion in which its immediate products survive in equilibrium. This matter will be probed further.

In the meantime let us calculate the self-dissociation at equilibrium on the assumption, which at least is approximately true, that it consists wholly of ionic self-dehydration. Then $[H_2NO_3^+] = 0$, and $[NO_2^+] = [NO_3^-] = [H_2O]$. From the temperature interval between the origin of the theoretical freezing-point curves and the observed maximum freezing point of nitric acid, we find

$$[NO_2^+] + [NO_3^-] + [H_2O] = 2{\cdot}20/2{\cdot}68 = 0{\cdot}82 \text{ molal}$$

and therefore

$$\left.\begin{array}{ll} [NO_2^+] = 0{\cdot}27 \text{ molal} = 1{\cdot}2\% \text{ by weight} \\ [NO_3^-] = 0{\cdot}27 \quad " \quad = 1{\cdot}7\% \quad " \quad " \\ [H_2O] = 0{\cdot}27 \quad " \quad = 0{\cdot}5\% \quad " \quad " \end{array}\right\} \text{Total dissociated} = 3{\cdot}4\%$$

Since we have estimated that each of the three products is solvated with two molecules of nitric acid, a further 10% of the nitric acid has to be pictured as being bound in solvates of the 3·4% of self-dissociation products. The value of the equilibrium constant for ionic self-dehydration is

$$K_{\text{ad}} = [NO_2^+][NO_3^-][H_2O] = 0{\cdot}020 \text{ g.-mol.}^3 \text{ kg.}^{-3}$$

Granted the basic assumption that the amount of autoprotolysis is small enough to be neglected, these values are expected to be more accurate than the estimates derived from Raman intensities. On the other hand, exact agreement could not be expected, even if both methods were quite accurate, because the present values apply to the temperature −40°, while the spectroscopic values relate to the temperature −15°.

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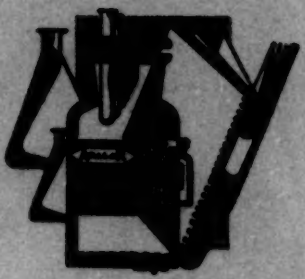

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